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PRACTICAL CHEMISTRY.

THE PRINCIPLES OF

QUALITATIVE ANALYSIS.

BY

WILLIAM A. TILDEN, D.Sc. LOND., F.R.S.

Professor of Chemistry in the Mason College, Birmingham;
Formerly Lecturer on Chemistry in Clifton College.

FOURTH EDITION.

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with which he will afterwards be constantly dealing; he also learns the use of the Blowpipe.

The second part is devoted to methods of Analysis. Here he is first instructed in the properties of a few of the constituents of common salts, and is taught methods for their separation or identification in presence of one another. If he goes no further than this he will at least have learnt what chemical analysis means. He afterwards proceeds to extend his knowledge, till at the end of the course he will be able to analyse any mixture of ordinary inorganic substances.

The analytical part is to a great extent shorn of directions for manipulation, as well as of details which are not relevant to the immediate object of the experiment. According to my experience these are not only of no use, but are a positive hindrance to the apprehension of the facts to be acquired. Manipulation can only be learnt properly under personal instruction by a competent teacher, and more will be accomplished by letting the beginner *see* once for all how a thing is to be done than by whole volumes of printed directions.

W. A. T.

CLIFTON : *January* 1880.

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PRACTICAL CHEMISTRY.

PART I.

PRELIMINARY.

To make a Washing Bottle.—Take a clean wide-mouth bottle, holding about a pint, and fit a good sound cork tightly into the neck. Then take a piece of stout glass tubing (about $\frac{1}{4}$ inch external diameter) and, with the aid of a cork borer, bore two holes through the cork, parallel to each other and of such a size that the tube will pass through with some friction. If you have not a cork borer of the exact size required, take one a little smaller and then enlarge the hole by means of a round file. Cut off a piece of the tube of about twice the height of the bottle. Draw off one end to a point in the blowpipe flame. Cut it off with a file and make the orifice smooth by holding it in the flame for a minute or two, taking care not to close it completely. Then, in a common fish-tail gas flame, bend the tube so as to

form an angle of about 60° at such a distance from the wide end that when the tube is passed through the cork it will reach well to the bottom of the bottle. Into the second hole in the cork another piece of the same tubing is fitted, but this is cut off just below the cork, and is bent to form an angle of about 120°. The open end, projecting upwards, should be made smooth at the edge, by holding it for a few minutes in a Bunsen flame. The whole arrangement is shown in the figure, and will be sufficiently intelligible. Fill the bottle with distilled water, and it is ready for use. The object of this apparatus is to enable the operator to send a stream of water upon a precipitate contained in a filter, or to deliver small quantities of water into test tubes and for general purposes as a store of water. It is used by blowing gently into the upturned end of the mouthpiece, and so producing a pressure upon the surface of the water in the bottle.

FIG. 1.

To Fix a Platinum Wire into a Glass Holder.—Take six inches of narrow glass tubing, and by holding it in the Bunsen flame soften it so that it may be drawn out in the middle. When cold, scratch it at the middle with a file and break it into two. Insert into the narrow end of one half a piece of

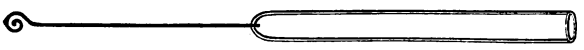
form an angle of about 60° at such a distance from the wide end that when the tube is passed through the cork it will reach well to the bottom of the bottle. Into the second hole in the cork another piece of the same tubing is fitted, but this is cut off just below the cork, and is bent to form an angle of about 120°. The open end, projecting upwards, should be made smooth at the edge, by holding it for a few minutes in a Bunsen flame. The whole arrangement is shown in the figure, and will be sufficiently intelligible. Fill the bottle with distilled water, and it is ready for use. The object of this apparatus is to enable the operator to send a stream of water upon a precipitate contained in a filter, or to deliver small quantities of water into test tubes and for general purposes as a store of water. It is used by blowing gently into the upturned end of the mouthpiece, and so producing a pressure upon the surface of the water in the bottle.

FIG. 1.

To Fix a Platinum Wire into a Glass Holder.—Take six inches of narrow glass tubing, and by holding it in the Bunsen flame soften it so that it may be drawn out in the middle. When cold, scratch it at the middle with a file and break it into two. Insert into the narrow end of one half a piece of

platinum wire about two inches long, and holding the wire and tube steadily together, heat again at the same point till the glass closes round the wire. The figure shows the result.

FIG. 2



The tube should be stuck into a flat cork, and by it the end of the wire suspended in some dilute hydrochloric acid contained in a test tube. If kept in this way, the wire will always be clean and ready for use.

PROPERTIES OF SOME IMPORTANT SUBSTANCES IN DAILY USE.

Distilled Water.—For analytical purposes common water drawn from the tap is always too impure. It holds in solution calcium carbonate, calcium chloride, and calcium sulphate, besides other compounds which produce marked effects upon the reagents, and would, if water containing them were used, lead to confusion.

Try the following *experiments*:—

1. Mix in a test tube some common water with a little pure nitric acid and some solution of nitrate of silver. A white precipitate of chloride of silver generally results. Distilled water treated in the same way should remain quite clear, showing that it is free from chlorides.

2. Mix in a test tube some common water with a little hydrochloric acid and some chloride of barium. A white precipitate of sulphate of barium generally appears. Distilled water should give no such precipitate.

3. Boil some common water in a flask for about five minutes. It usually becomes cloudy, and deposits a gritty powder upon the flask. This cloudiness is due to the precipitation of calcium carbonate, which in the natural water is held in solution by carbonic acid. As soon as the carbonic acid is decomposed, and the carbon dioxide expelled by heat, the calcium carbonate is thrown down, as it is not appreciably soluble in water.

Distilled water when boiled remains clear.

4. Add to some distilled water a little solution of soap and shake it. It froths or 'lathers' immediately. Distilled water is very 'soft.'

Soap solution added to common water makes it cloudy, and no 'lathering' will be possible till a considerable quantity of soap has been added. Common spring or river water is generally 'hard.' The hardness is due to the salts of calcium and magnesium present, as these salts decompose the soap and form insoluble compounds. After common water has been boiled, and the precipitated calcium carbonate filtered off, the water will be found to be softer than before. The hardness due to the presence of calcium carbonate dissolved in carbonic acid is said to be 'temporary

hardness,' whilst that which is owing to the presence of calcium or magnesium chloride or sulphate is called 'permanent hardness,' because it cannot be removed by simple boiling.

5. Distilled water should be devoid of taste and smell, and when evaporated to dryness should leave no residue. Evaporate a few drops of distilled water on a platinum capsule. No stain will be visible. Now evaporate about the same quantity in a glass or porcelain dish. A perceptible residue will be seen, but this is due to the action of the water on the glass or porcelain surface.

Sulphuric Acid, H_2SO_4.—A colourless oily liquid, hence often called 'oil of vitriol,' of specific gravity 1.84, which when poured into water generates much heat.

The following *experiments* may be tried :—

1. Dilute some oil of vitriol with about ten times its bulk of water, pouring the acid into the water. By means of a brush draw some characters upon a sheet of paper with this diluted acid, and then dry the sheet either before a fire or over a hot plate. As the water evaporates away the strong acid which remains chars and blackens the paper. Strong sulphuric acid is very corrosive, and rapidly destroys all kinds of organic matter. If splashed upon the clothes it generally produces a red stain, and afterwards a hole. Such spots, if accidentally produced, should be wetted with water immediately, and as soon as possible with solution of ammonia.

2. Into the diluted acid drop a piece of copper. No action occurs. Now add to another portion a piece of granulated zinc. A rapid effervescence immediately begins, owing to the escape of hydrogen gas, and, if the experiment be made in a test-tube, the gas may be burnt at the mouth of the tube. After standing for half an hour crystals of zinc sulphate, $ZnSO_4.7OH_2$, will be deposited from the solution. Zinc and iron dissolve in diluted sulphuric acid forming soluble sulphates, and evolving hydrogen. Copper, mercury, and lead are not appreciably affected by the diluted acid.

3. Place in a test tube a few scraps of clean copper, add a little strong sulphuric acid, and heat gently in the fume closet. Effervescence soon begins and sulphur dioxide escapes. After the action is over add some water to the dark-coloured mass and filter the solution. A blue liquid is obtained, from which, by evaporating in a porcelain dish, blue crystals of copper sulphate, $CuSO_4.5OH_2$, may be produced.

The action of the copper on the sulphuric acid is probably first of all

$$Cu + H_2SO_4 = CuSO_4 + 2H.$$

But the hydrogen never escapes, for at the moment of its liberation it acts upon another portion of the sulphuric acid and reduces it.

$$2H + H_2SO_4 = 2OH_2 + SO_2.$$

So that the gas actually evolved is sulphur dioxide. Mercury behaves in the same way as copper.

Sulphuric acid may contain impurities, the chief of which may be recognised as follows :—

4. When sulphuric acid is poured into water it should not deposit any white precipitate of lead sulphate, $PbSO_4$, or mere traces only.

5. Sulphuric acid should be free from nitrosyl sulphate, $NOHSO_4$. Make a solution of ferrous sulphate in water, and when quite cold pour it into a test tube containing a little strong sulphuric acid in such a way that the liquids do not mix. No dark coloration should be produced in either of them near the surface of contact. Any purple or brown colour would indicate the formation of a compound of nitric oxide, NO, with ferrous sulphate, $FeSO_4$.

Nitric Acid, HNO_3.—Ordinary nitric acid has a specific gravity 1.42, and contains 70 parts of real nitric acid, HNO_3, to 30 parts of water. It is a colourless liquid, miscible with water in all proportions and producing some heat in the process. It often exhibits a small amount of yellow vapour, NO_2, especially after exposure to light. It stains the skin yellow. Spots produced by nitric acid upon the clothes cannot be restored to their original colour by the application of ammonia, but should always be wetted with it, or a hole will probably result.

Try the following *experiments* :—

1. Pour a little nitric acid upon a few scraps of

copper, or almost any other metal, contained in a test tube. Deep yellow fumes are produced. The action which occurs is explained thus : In the first place the metal displaces hydrogen from part of the acid.

$$Cu + 2HNO_3 = Cu(NO_3)_2 + 2H.$$

The nascent hydrogen attacks another portion of nitric acid immediately, and one of the oxides of nitrogen is evolved.

$$6H + 2HNO_3 = 4OH_2 + 2NO.$$

If we suppose nitric oxide, NO, to be formed, the production of coloured gas is accounted for by the union of the nitric oxide with oxygen taken from the air.

Notice that hydrogen is never evolved from nitric acid.

2. Diluted with water and mixed with nitrate of silver, nitric acid should give no precipitate, showing its freedom from hydrochloric acid.

3. Nitric acid should also be free from sulphuric acid, and should therefore give no precipitate with barium chloride. It must be freely diluted with water before applying the test, or a precipitate of *nitrate* of barium may be formed.

Hydrochloric Acid.—Solution of HCl. The ordinary fuming hydrochloric acid is a solution in water containing about one-third of its weight of HCl. The specific gravity of the liquid is 1.16.

The liquid should be colourless, and after dilution

with water should give no precipitate with barium chloride or sulphuretted hydrogen. Absence of sulphuric acid and of arsenic is thus proved.

Experiments:—

1. Add a piece of granulated zinc to some hydrochloric acid. The metal quickly dissolves, whilst hydrogen, recognisable by its inflammability, escapes. Iron behaves in the same way.

2. Copper and mercury are not perceptibly affected by hydrochloric acid.

3. Add to a third portion of hydrochloric acid in a test tube a few grains of black oxide of manganese. Chlorine will be evolved, especially when a gentle heat is applied. The gas is easily recognised by its yellow colour, disagreeable and suffocating smell, and by bleaching a piece of coloured calico or litmus paper held in it.

Aqua Regia is a mixture of nitric acid with about three times its bulk of strong hydrochloric acid. When heated it evolves chlorine and a yellow gas, nitrosyl chloride, produced according to this equation :—

$$3HCl + HNO_3 = Cl_2 + NOCl + 2OH_2.$$

Aqua regia is used for dissolving metals, such as gold and platinum, which are not soluble in hydrochloric or nitric acid, also for dissolving certain sulphides—e.g. HgS, NiS, CoS, &c. It converts all metals into chlorides.

Acetic Acid.—$C_2H_4O_2$, or $HC_2H_3O_2$. In the pure state, unmixed with water, acetic acid is a crystallisable solid which melts at 17°. In this state it is known as 'glacial' acetic acid. Ordinary strong acetic acid contains about one-third of its weight of real acid. It is a colourless liquid, having a strong smell of vinegar, and should give, when diluted with water, no precipitate with chloride of barium, with nitrate of silver, or with sulphuretted hydrogen. The first of these tests indicates the absence of sulphuric acid, the second the absence of hydrochloric acid, whilst the last shows that the acetic acid is free from metals such as copper.

Acetic acid dissolves iron and zinc, evolving hydrogen, but less rapidly than hydrochloric or diluted sulphuric acid.

Solution of Soda or Sodium Hydroxide.—Caustic soda, NaHO, is a white deliquescent solid. The solution is usually made by dissolving one part of it in twenty parts of water. It produces a soapy sensation when rubbed between the finger and thumb.

The solution neutralises all acids, and has a strongly alkaline reaction—that is, it changes the colour of red litmus to blue and of vegetable red* to green.

Experiments :—

1. Both solid sodium hydroxide and its solution in

* Tincture of red cabbage, of hollyhock, or dahlia flowers, &c.

water absorb carbon dioxide from the air, and hence after exposure always contain more or less carbonate of sodium. The solution, when quite free from carbonate, gives no precipitate when mixed with lime water, but it usually does give a small precipitate. It ought not, however, to effervesce freely with excess of hydrochloric acid, for that would indicate the presence of too much carbonate..

2. Sodium hydroxide added to the salts of metals produces precipitates, consisting of hydroxides of those metals or oxides. These hydroxides are for the most part easily resolved, by heating, into water and the oxide of the metal, the decomposition being sometimes attended by characteristic changes of colour.

Add solution of sodium hydroxide to solution of ferric chloride; brown ferric hydroxide ($Fe_2H_6O_6$) is thrown down. Add solution of sodium hydroxide to solution of copper sulphate; blue copper hydroxide, $Cu(HO)_2$, is thrown down. Boil the liquid; the blue precipitate becomes black (CuO). Add solution of sodium hydroxide to mercuric chloride; yellow mercuric oxide, HgO, is precipitated. Add solution of sodium hydroxide to solution of silver nitrate; dark brown silver oxide, Ag_2O, is precipitated.

3. Sodium hydroxide saponifies fats. Boil in a test tube some solution of soda with a few drops of olive oil for about five minutes. The oil will gradually dissolve, forming a solution of common soap.

$$C_3H_5(C_{18}H_{33}O_2)_3 + 3NaHO$$

Glyceric oleate (olive oil)

$$= C_3H_5(OH)_3 + 3NaC_{18}H_{33}O_2.$$

Glycerine — Sodium oleate (hard soap).

On adding a little common salt to the liquid, the soap separates and rises to the surface. The glycerine, together with excess of soda and common salt, remains in solution.

Potassium Hydroxide.—KHO. Resembles sodium hydroxide in nearly every respect.

Solution of Ammonia, or Ammonium Hydroxide. Ammonia, NH_3, is a colourless gas which has an intensely pungent smell, and is very soluble in water. The strongest solution made by the manufacturer contains nearly one-third of its weight of the gas, which at common temperatures is constantly escaping from it. In the summer time it is necessary to keep the bottles only partly filled and stored in a cool place, or they might burst. The ordinary solution required as a reagent is made by mixing this strongest solution with twice its bulk of distilled water. Both solutions smell strongly of the gas, and produce a very alkaline reaction with vegetable colours. It is usual to consider that the liquid contains a compound, called ammonium hydroxide, which consists of the elements of ammonia united to those of water, and is similar in constitution to the hydroxides of potassium and sodium.

Potassium hydroxide, or caustic potash.	Sodium hydroxide, or caustic soda.	Ammonium hydroxide, or solution of ammonia.
KHO.	NaHO.	NH_4HO.

Experiments:—

1. When solution of ammonium hydroxide is evaporated to dryness nothing remains. Ammonium hydroxide is not known in the solid state.

2. The solution behaves in many respects like solution of sodium hydroxide, but in others it differs from it. Thus when added to solution of ferric chloride it throws down the brown ferric hydroxide, but when added to mercuric chloride it gives a white precipitate ($HgNH_2Cl$); to silver nitrate a brown precipitate, which redissolves in excess; to copper sulphate a pale blue precipitate, which is easily soluble in excess of ammonia, forming a magnificent blue liquid.

3. Ammonia neutralises all acids, but it does not readily saponify fat.

4. The impurity usually present in solution of ammonia, is tarry matter, the smell of which becomes perceptible when the liquid is neutralised by hydrochloric or dilute sulphuric acid. The addition of a slight excess of acid not unfrequently produces a pink colour, which is due to the presence of a coal-tar base, derived from the ammoniacal gas-liquor from which the ammonia was indirectly prepared.

Lime and Lime Water.—Quicklime, CaO, is a white, or slightly grey, earthy-looking substance, which,

when heated as strongly as possible in the blowpipe flame, does not melt, but gives out a brilliant white light.

Experiments :—

1. Place a small lump of quicklime on a plate and sprinkle it with water, a few drops at a time. It soon grows hot and steam rises from it. Continue adding small quantities of water till the mass crumbles away into a soft white powder. This is calcium hydroxide, $CaO + OH_2$ or $Ca(HO)_2$, commonly called slaked lime.

2. Shake up some slaked lime in a large bottleful of water. Let the turbid liquid rest till it becomes quite clear. Then pour it off the undissolved portion. The solution is called lime water. It is a weak solution containing about one part of calcium hydroxide in one thousand of water.

3. Lime water is alkaline, and turns red litmus blue. It also produces precipitates of hydroxides when added to metallic salts. In this respect it behaves precisely like a weak solution of soda. (See Sodium Hydroxide.)

4. The chief use of lime water is to detect carbonic acid gas. By means of a clean piece of tubing blow air from the mouth through some clear lime water. A white precipitate of calcium carbonate is formed, showing the presence of carbon dioxide in the expired air.

Sulphuretted Hydrogen or Hydrogen Sulphide.—H_2S. The materials used for generating sulphuretted hydrogen are ferrous sulphide, in lumps, and diluted hydrochloric or sulphuric acid.

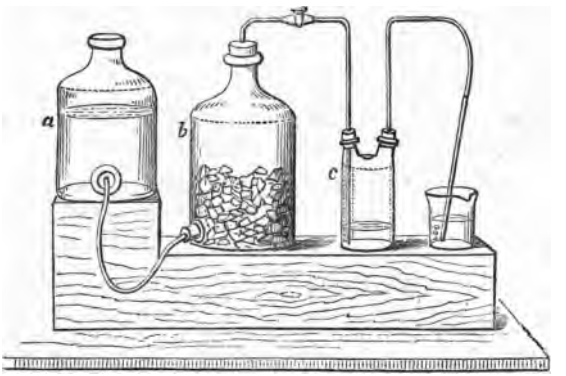
$$FeS + 2HCl = FeCl_2 + H_2S,$$

or

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

As this gas is an indispensable agent, and is very frequently required, it is necessary to have some form of apparatus by which a supply may be obtained at a moment's notice. Such an apparatus will be found in every laboratory where analytical work is done.

FIG. 3.



One of the simplest and most convenient arrangements is shown in fig. 3.

a and *b* are two bottles having an additional neck at the side near the bottom. Into *b* is first put a quantity of glass marbles or old stoppers, so as to form a layer rather more than an inch deep. Upon this glass foundation is laid the sulphide of iron in

lumps. *a* and *b* are connected together by a piece of india-rubber tubing, and *b* communicates, by a tube having a stop-cock, with a small Woulff's bottle, *c*, containing a little water. A sufficient quantity of hydrochloric acid, diluted with rather more than an equal bulk of water, is poured into *a*, and when it is desired to generate the gas, this bottle is lifted up and placed upon the block of wood, so that it stands at a higher level than *b*. On turning the stop-cock the acid flows down upon the sulphide of iron and generates the sulphuretted hydrogen, which is driven through the water in the wash-bottle into the solution or vessel where it is required. When the gas is no longer wanted, the stop-cock should be closed and bottle *a* replaced upon the table.

Sulphuretted hydrogen has a most disagreeable smell, and, as it is undoubtedly poisonous when inhaled to any extent, students should as much as possible be careful to avoid letting it escape. All operations with the gas must be conducted in the draught cupboard. When any considerable quantity of substance has to be exposed to the action of this reagent, as in separating metals, it is necessary to pass the gas in bubbles through the solution. But when the object is merely to see what effect, if any, is produced by sulphuretted hydrogen upon the liquid to be tested, it is much more convenient to use a solution of the gas in water. This is made by causing the gas to bubble slowly through a quantity of distilled water for an

hour or more, shaking the liquid from time to time. Water will dissolve about three times its volume of sulphuretted hydrogen at ordinary temperatures ; but the solution generally contains less than this, and tends to grow weaker after a time, especially when the bottle is frequently opened. The loss is partly due to escape of the gas into the air, and partly to the oxidation of the dissolved portion by the oxygen of the air, white sulphur being at the same time deposited. It should be remembered that under any circumstances the solution will contain very little sulphuretted hydrogen, and therefore it should be added pretty freely to the liquid which is to be tested. The action of sulphuretted hydrogen gas upon a solution of a metal depends upon circumstances. It is capable of acting two parts, behaving with certain solutions merely as a reducing agent in virtue of the hydrogen it contains, or more generally causing the formation of the sulphide of the metal. As instances of these two modes of action the following *experiments* may be made :—

1. Pass the gas into an acidified solution of ferric chloride ; white sulphur will be thrown down and the yellow colour of the liquid will disappear.

$$\underset{\text{Ferric chloride.}}{Fe_2Cl_6} + H_2S = \underset{\text{Ferrous chloride.}}{2FeCl_2} + 2HCl + S.$$

No sulphide of iron is formed, because it is soluble in acids.

2. Pass sulphuretted hydrogen into solution of

zinc sulphate mixed with some hydrochloric acid. No visible effect will be produced, because zinc sulphide is soluble in acids.

3. Pass sulphuretted hydrogen into solution of the same salt previously mixed with excess of ammonia. A white precipitate of zinc sulphide will be formed.

4. Pass sulphuretted hydrogen into an acidified solution of copper sulphate. A brown or nearly black precipitate of cupric sulphide will be thrown down, and on filtering the liquid, after completely saturating with the gas, it will be found to be colourless and to contain no copper.

Thus it appears that sulphuretted hydrogen is capable of precipitating certain metals as sulphides from the solutions of their salts mixed with acid, whilst the sulphides of other metals are not formed under such circumstances, but only in the presence of alkalies. There is yet another class whose sulphides are soluble in water, and hence are never precipitated under any circumstances; such, for example, are the metals of the earths, Ba, Sr, Ca, Mg, and of the alkalies K, Na, NH_4.

Solution of Ammonium Sulphide.—When freshly made, by passing sulphuretted hydrogen gas into ordinary solution of ammonia, this solution is quite colourless, and may be regarded as a substitute for sulphuretted hydrogen when sulphides are to be precipitated from an alkaline solution.

Experiments :—

1. Add solution of ammonium sulphide to solution of sulphate of zinc ; white zinc sulphide is precipitated.

2. Add ammonium sulphide to solution of ferrous sulphate ; black iron sulphide is thrown down.

3. Add ammonium sulphide to solution of manganous chloride ; pink manganous sulphide is thrown down.

Colourless ammonium sulphide contains NH_4HS or $(NH_4)_2S$, according as the solution has been prepared with excess of sulphuretted hydrogen or not. After exposure to the air for a time it becomes yellow from oxidation, and then contains, besides ammonium theiosulphate, $(NH_4)_2S_2O_3$, and ammonium sulphate, $(NH_4)_2SO_4$, a polysulphide of ammonium, which we will represent as $(NH_4)_2S_2$. This yellow solution is used for the purpose of dissolving certain sulphides, especially the sulphides of arsenic, antimony, and tin. The solutions thus formed contain sulphur salts, from which the metallic sulphides are thrown down again on addition of acids.

Experiments :—

1. Pass sulphuretted hydrogen into a solution of arsenious chloride, and filter off the yellow precipitate of arsenious sulphide, As_2S_3, which is thrown down. Wash the precipitate, and then boil some of it with yellow sulphide of ammonium.

It dissolves, and the solution contains a sulpharsenite or sulpharsenate of ammonium.

$$3(NH_4)_2S + As_2S_3 = 2(NH_4)_3AsS_3,$$

or

$$3(NH_4)_2S + As_2S_3 + S_2 = 2(NH_4)_3AsS_4.$$

On the addition of hydrochloric acid in excess the same yellow sulphide is thrown down, either alone or mixed with sulphur, sulphuretted hydrogen escapes, and chloride of ammonium remains in solution. Thus :—

$$2(NH_4)_3AsS_3 + 6HCl = 6NH_4Cl + 3H_2S + As_2S_3,$$

or

$$2(NH_4)_3AsS_4 + 6HCl = 6NH_4Cl + 3H_2S + As_2S_3 + S_2.$$

2. Yellow ammonium sulphide is decomposed by acids, yielding a white precipitate of sulphur.

$$(NH_4)_2S_2 + 2HCl = 2NH_4Cl + H_2S + S.$$

Potassium Chlorate.—$KClO_3$. A colourless salt forming flat crystals.

Experiments :—

1. Boil some potassium chlorate in a test tube with about six times its weight of water till dissolved, and let the solution cool. It deposits sooner or later thin flat rhomboidal crystals, which do not dissolve in less than about twenty times their weight of cold water.

2. Heat a few crystals of potassium chlorate in a test tube. The salt first decrepitates (crackles), then melts and boils from escape of oxygen gas. Test for the oxygen in the tube by lighting a match, and, after letting it burn for a few seconds, blowing it out, and introducing the red-hot tip into the mouth of the test tube. The match bursts into flame.

3. Let the salt cool. It sets into a solid opaque mass. Boil this in water till dissolved, and allow the solution to cool. It will deposit small granular crystals of potassium perchlorate, whilst potassium chloride remains in solution.

Action of heat on potassium chlorate :—

1st stage—

$$2KClO_3 = KCl + KClO_4 + O_2.$$

2nd stage—

$$KCl + KClO_4 = 2KCl + 2O_2.$$

Potassium chlorate is, therefore, ultimately decomposed into oxygen and potassium chloride. This, however, requires a strong heat.

Potassium Nitrate.—(Nitre or saltpetre) KNO_3. Potassium nitrate is a colourless salt which crystallises in large prismatic crystals. It is easily soluble in water.

Experiments :—

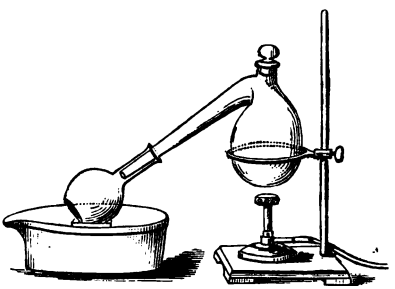
1. Place about two ounces of powdered nitre in a glass retort, and pour on it one ounce by measure of strong sulphuric acid. On applying a gentle heat

nitric acid distils over into the flask, which serves both as condenser and receiver. The arrangement of the apparatus is shown in the figure.

The flask is kept cool by laying upon it a piece of filter paper, which is wetted from time to time with cold water.

When the nitric acid ceases to come over, the retort is allowed to cool, and the residue sets into a mass of crystals consisting of potassium hydrogen sulphate, $KHSO_4$.

FIG. 4.



2. Dip a piece of filter paper into a solution of nitre and then dry it. On applying a spark to the paper it ignites and rapidly smoulders away. Nitre readily communicates oxygen to combustible matters, and if used in sufficient quantity, will enable them to burn without assistance of air. With charcoal and sulphur it is an ingredient of gunpowder. (See also Blowpipe, p. 33, and p. 28.)

Ammonium Chloride, or Sal-Ammoniac.—NH_4Cl. Crystalline masses, tough and difficult to powder. Soluble in water; the solution neutral to test papers.

Experiments:—

1. Heat a piece the size of a pea in a dry test tube. It does not melt, but sublimes completely.

2. Boil some sal-ammoniac with about three times its weight of water, and allow the solution to cool. Crystals are deposited having the appearance of stars and fern-leaves.

Ammonium Carbonate.—Colourless hard crystalline masses smelling strongly of ammonia. Soluble in water, the solution being strongly alkaline.

Experiment.—Heat a small lump in a test tube. It evaporates away, leaving upon the sides of the tube only a small liquid sublimate, which crystallises on cooling.

Sodium Carbonate.—Na_2CO_3. This salt may be obtained by drying common soda crystals, $Na_2CO_3.10OH_2$, and rubbing the mass to powder; but it is best made by heating, in a porcelain dish, over a lamp, the 'bicarbonate' or acid carbonate of sodium, $NaHCO_3$.

Experiments:—

1. Melt some sodium carbonate on a loop of platinum wire, or in a platinum capsule, by holding it in the Bunsen flame. The melted mass on cooling forms an opaque white mass, unlike melted borax, which is clear.

2. Re-melt the opaque mass just obtained, and

when melted add some white sand in small quantities at a time. The mass effervesces, and when a sufficient quantity of sand has been added it will be found that the mass is much less easily fusible, requiring a much stronger heat to keep it liquid. On cooling it remains clear. It is now glass, differing from common glass chiefly in containing a much larger proportion of alkali, but agreeing in all essential characters.

3. Place a few crystals of washing soda at the bottom of a cylindrical gas jar, and pour over them a small quantity of dilute sulphuric acid. The gas which escapes with effervescence soon fills the jar, and will be found to extinguish a lighted candle. Being much heavier than air, the gas may be poured into another cylinder containing some lime water, which, on shaking, will become milky. The gas is carbon dioxide or carbonic anhydride.

Potassium Cyanide.—This salt is usually met with in deliquescent lumps, evidently consisting of portions of a fused mass. The common cyanide is made by melting in a crucible a mixture of dry ferrocyanide and carbonate of potassium, and pouring out the salt, whilst still liquid, upon a stone. The reaction which occurs is as follows :—

$K_4FeC_6N_6$	+	K_2CO_3	=	$5KCN.$
Potassium ferrocyanide.		Potassium carbonate.		Potassium cyanide.

$+KCNO$	+	Fe	+	$CO_2.$
Potassium cyanate.		Metallic iron.		Carbonic anhydride.

The carbonic anhydride escapes in the gaseous form; the metallic iron remains in the form of a spongy mass at the bottom of the crucible. So that commercial cyanide of potassium is a mixture of cyanide with cyanate and a large quantity of carbonate, which may be regarded as an adulteration. Nevertheless the presence of these other salts in no way interferes with the use of the cyanide as a reducing agent before the blowpipe. (See p. 34.)

But in the separation of cobalt and nickel (p. 54) it is necessary to use pure potassium cyanide. This may be purchased, or in place of it a mixture of hydrocyanic acid (prussic acid) and caustic potash or soda serves equally well.

Remember that *all cyanides*, and especially prussic acid and the alkaline cyanides, are *very poisonous*.

Experiments:—

1. Melt some cyanide of potassium in an iron spoon, and add to it a small quantity of oxide of lead. On cooling the mass and boiling it in water the salt will dissolve and leave a button of metallic lead.

KCN	+	PbO	=	KCNO	+	Pb.
Potassium cyanide.		Litharge.		Potassium cyanate.		Lead.

Cyanide of potassium in the melted state is a powerful reducing agent, and is used as such in the detection of metals.

2. Boil a small piece of cyanide of potassium

with water and a pinch of flowers of sulphur. After a few minutes filter the solution. It now contains theiocyanate (sulphocyanide) of potassium, and when slightly acidified with hydrochloric acid and mixed with solution of ferric chloride gives a red colour.

Borax.—$Na_2B_4O_7.10OH_2$. Borax forms large crystals, which contain a great deal of water. It is soluble in water, and is alkaline to test paper.

Experiments:—

1. Heat some borax in a platinum capsule. It first swells up during the escape of water vapour, and after a time melts down into a clear glass, $Na_2B_4O_7$. This melted anhydrous borax dissolves most metallic oxides, in many cases assuming characteristic colours. Add to it a small particle of a cobalt salt and melt again. The mass becomes clear blue. Borax is used in many blowpipe experiments.

2. Make a pretty strong solution of borax in a test tube by boiling with water, and whilst hot acidify the liquid with hydrochloric acid. On cooling, scaly crystals of boric acid, H_3BO_3, are deposited. Collect these crystals on a filter, wash them with a little water, and boil in a clean test tube with methylated spirit. They will dissolve, and if the solution is ignited it burns with a peculiar green flame.

Microcosmic Salt.—Sodium ammonium hydrogen phosphate, $NaNH_4HPO_4.4OH_2$.

Colourless very fusible crystals.

Experiments:—

1. Dissolve a particle in distilled water and add solution of silver nitrate. A yellow precipitate is produced, consisting of silver orthophosphate, Ag_3PO_4.

2. Heat a crystal on a loop of platinum wire, or more conveniently on a platinum capsule, till it melts down into a clear glass. Dissolve this in water in a test tube and add to the solution some silver nitrate. A white precipitate of silver metaphosphate, $AgPO_3$, ensues. Fusion of microcosmic salt causes it to give off its water of crystallisation and ammonia, and ultimately to leave only sodium metaphosphate, $NaPO_3$. Fused sodium metaphosphate is often used in blowpipe experiments for dissolving various metallic oxides.

Test Papers.—Litmus paper is paper which has been stained with a solution of litmus. There should be three kinds. Red litmus is used for recognising alkaline salts and solutions. It is turned blue by them. Blue litmus paper in contact with an acid or acid salt becomes red. Mauve or violet litmus paper is nearly neutral, and is used in those cases in which the acid or alkaline reaction is too feeble to cause a marked change in paper which is decidedly red or blue. Try the action of litmus papers with the following substances, and see that they are respectively acid, neutral, and alkaline:—

Acid.—Blue litmus becoming red. Dilute H_2SO_4,

dilute HCl, dilute HNO_3, and solution of $NaHC_4H_4O_6$.

Neutral.—No change. Solution of NaCl, of KNO_3, and of Na_2SO_4.

Alkaline.—Red litmus becoming blue. Solution of NaHO, of NH_4HO, and of $Ca(HO)_2$; also solutions of the salt Na_2HPO_4, and borax, $Na_2B_4O_7$.

Turmeric paper is yellow, is unaltered by ordinary acids, but becomes brown when wetted with an alkaline solution.

Paper wetted with lead acetate is often used as a test for H_2S. The brown or black stain formed consists of lead sulphide.

Paper is also used as a means of exposing several other reagents to the action of gases, not because there is any special virtue in paper, but because in this way very slight changes of colour become perceptible.

Charcoal.—Wood charcoal is used as a support for substances exposed to the blowpipe flame when reducing effects are desired. Notice that it exhibits the structure of the wood very plainly, although it weighs much less, and consists, practically speaking, of carbon. Direct the blowpipe flame upon a small crystal of nitre placed upon a piece of charcoal, and notice that when the salt melts it causes deflagration—that is, vivid combustion with sparks. The white mass which remains consists of potassium carbonate. Pick it off, place it in a test tube with some dilute

acid of any kind, and notice that it effervesces from escape of CO_2. Charcoal, when heated upon a platinum cup or foil, burns away, leaving a very light, grey or reddish-coloured, ash. Powdered charcoal may be recognised by applying these tests.

Sulphur.—Sulphur is very seldom required as a reagent, but it makes its appearance so often in analytical experiments that the student must be able to recognise it under its various disguises. In its common form it is a yellow, very brittle solid.

Experiments:—

1. Heat some sulphur gently in a dry test tube. It melts and forms a yellow liquid, which solidifies on cooling, forming a mass of yellowish waxy-looking prismatic crystals.

2. Raise the temperature of the melted sulphur. At a certain point it becomes dark-coloured and so viscid as almost to solidify; but when heated still more strongly it becomes again partly liquefied, and if when in this state it is poured into cold water it yields an elastic stringy mass.

3. Heated still further, the melted sulphur boils and evolves a brown very inflammable vapour.

4. Heat a small piece of sulphur in a spoon. It readily takes fire in the air, burning with a very pale blue light and emitting sulphur dioxide gas, the smell of which is characteristic.

5. Sulphur is insoluble in water. Dissolve a small piece of sulphur in some carbon bisulphide

pour out the solution into a small beaker, and cover it with paper. In a short time the liquid will have evaporated away, leaving the sulphur in the form of transparent pale yellow octahedral crystals.

6. Sulphur is insoluble in hydrochloric acid.

7. Boiled with common nitric acid, sulphur melts* and very slowly dissolves, giving sulphuric acid, which may be recognised by adding water and then solution of barium chloride.

Aqua regia dissolves sulphur in the same way.

8. Heated with strong sulphuric acid, sulphur melts and slowly dissolves, forming sulphur dioxide, which escapes.

$$S + 2H_2SO_4 = 3SO_2 + 2H_2O.$$

9. Boil some flowers of sulphur with solution of soda, and filter the yellow solution. It now contains sodium sulphide and theiosulphate, from which the sulphur is again thrown down as a white precipitate on adding an acid in sufficient quantity.

$$2Na_2S + Na_2S_2O_3 + 6HCl = 6NaCl + 3OH_2 + 4S.$$

This precipitate, collected and dried, is the 'milk of sulphur' of the shops.

The sulphur thrown down from yellow sulphide of ammonium by acids is of the same kind.

* Because the boiling point of the acid, 120°, is above the melting point of the sulphur, 115°.

A similar white precipitate is formed on adding sulphuretted hydrogen water to any liquid which contains an oxidising agent, such as ferric chloride, free chlorine, nitrous acid, chromic acid, &c. Such substances convert the hydrogen of the H_2S into water or hydrochloric acid, and the sulphur is liberated. Sulphur is also set free during the action of nitric acid upon many sulphides. Copper sulphide, for example, boiled with strong nitric acid gives a blue solution of copper nitrate, whilst the sulphur collects in the form of yellow beads, easily recognisable by their colour, fusibility, and combustibility.

THE USE OF THE BLOWPIPE.

It is absolutely necessary to learn to blow continuously and without getting out of breath.

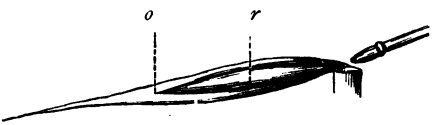
First close the lips and blow out the cheeks. Breathing can still be continued freely through the nose. After making this preliminary experiment once or twice it will be found that the introduction of a narrow glass tube between the lips will not cause the cheeks to collapse, although a stream of air issues through the tube. Now take the blowpipe between the lips, and blow steadily for a minute or two without permitting your breathing to be interrupted and keeping your cheeks well expanded.

Next direct the stream of air from the nozzle of the

pipe across a small flame and observe its appearance. It should form a straight, very tapering, and pointed blue cone 1½ inch or 2 inches long, burning quietly and steadily.

Experiments with the Blowpipe.—The blowpipe flame is used when it is required to observe the effects of a high temperature upon a substance, at the same time exposing it to contact with a stream of hot air in order to oxidise it, or to a stream of hot gas (consisting of compounds of carbon and hydrogen), so as to remove oxygen from it, or 'reduce'

FIG. 5.



it. The oxidising effects are produced by using a small flame, and introducing the substance, upon a loop of platinum wire, into the hot part near the tip of the flame (*o*). Reducing effects are obtained by increasing the quantity of gas till a slightly luminous streak (due to unburnt gas) is seen in the flame. The substance is then held in the inner part of the flame marked in figure (*r*).

Exp. 1. *Oxidation and Reduction.*—Heat the loop of platinum wire to redness and, whilst hot, dip it into powdered borax. Some of the salt will stick to it. Place this in the flame, and heat it till it ceases to swell up and finally melts down into a

clear glass-like bead. Touch this whilst hot with a particle of manganese chloride, the size of a pin's head, and transfer it to the oxidising flame. In about half a minute let it cool and look at it. It will have a purple colour, from the presence of a compound of manganese rich in oxygen. Now hold it in the reducing flame for about the same length of time. On cooling, the bead will be found colourless, the manganese having been reduced to manganous oxide.

Exp. 2. *Oxidation by Nitre.*—Make the platinum loop hot, and then dip it into some powdered KNO_3. Heat this till it just melts, and then dip it into some dry Na_2CO_3 or $NaHCO_3$. Melt the mass in the flame and let it cool. It should be quite white. Now attach to it a very small particle of chrome alum, and heat it till it melts in the flame. On cooling, the mass will be yellow, from the formation of potassium or sodium chromate. (For this experiment the heat of the Bunsen flame suffices.)

Exp. 3. *Reduction on Charcoal.*—Take a hard piece of charcoal and scrape a flat place or slight concavity upon one side; place upon this a very small heap of litharge, and direct upon it a reducing flame. In a few minutes it will melt, and in the melted mass will appear small globules of metallic lead.

Exp. 4. *Use of Flux.*—Mix some litharge with some dry Na_2CO_3, and heat as before on charcoal. Globules of lead will remain on the charcoal as before. The use of a fusible salt like sodium carbonate is

partly to prevent the compound from being absorbed by the charcoal, and partly to promote decomposition when such salts as sulphates, phosphates, &c., have to be operated upon.

Exp. 5. *Use of Cyanide of Potassium.*—Some metallic salts and oxides are not easily reducible by charcoal alone. Place a little tin dioxide on the charcoal, cover it with powdered KCN, and melt in reducing flame. White globules of tin are formed.

Exp. 6.—The globules or scales of metal are sometimes very small, and cannot be melted together so as to give larger ones. The following is an example of the mode of proceeding when such is the case :—Powder some ferrous sulphate and mix with it several times its weight of sodium carbonate and a little powder of charcoal; moisten slightly with water and heat a lump of the mixture supported upon charcoal in the reducing flame. The mass melts and boils, the escaping bubbles of gas (CO) generally burning upon the surface. After a minute or two cool, take off the fused mass, powder it in a small mortar, and stir up the powder with water. The particles of iron present are much heavier than the charcoal, and tend to sink much more rapidly. After allowing time for some of the black matter to subside, pour off the rest with the water. Repeat this process once or twice. Lastly pour the remaining powder with a little water into a watch-glass, or small beaker, or test tube, and place this over the pole of a magnet. In a few minutes the particles of

iron collect round the pole, and may be recognised by forming a sort of little beard, which falls away when the magnet is withdrawn.

Note.—In blowpipe experiments charcoal is the best support for the substance when the object is reduction, but it must not be used when the substance is to be oxidised either by the flame or by fusion with nitre. The platinum loop should be used in such cases, or occasionally a piece of platinum foil.

PREPARATION OF REAGENTS.

By a reaction is understood some chemical change which ensues when two or more substances, solid, liquid, or gaseous, are brought into contact with one another. A reagent is a substance which is added to another, under certain prescribed conditions, as a test, with the object of observing its effect upon that substance. By watching the changes, if any, which ensue, the chemist is enabled to learn something of the nature and composition of the substance under examination. The student is seldom required to prepare reagents for use; nevertheless it is essential that he should know the nature of substances that he has to deal with in almost every analytical operation he performs. A list is therefore given, in the next few pages, of the most useful reagents, together with short instructions for the preparation of most of them.

1. *Distilled Water.* This is always to be used for chemical purposes instead of common water.

2. *Strong Sulphuric Acid.*

3. *Dilute Sulphuric Acid.*—Pour 100 c.c. strong acid into 900 c.c.* water.

4. *Strong Hydrochloric Acid.*

5. *Dilute Hydrochloric Acid.*—Mix 300 c.c. strong acid with 700 c.c. water.

6. *Strong Nitric Acid.*

7. *Dilute Nitric Acid.*—Mix 200 c.c. strong acid with 800 c.c. water.

8. *Acetic Acid.*—Mix 500 c.c. ordinary commercial strong acetic acid (sp. grav. 1.044) with 500 c.c. water.

9. *Solution of Soda, or Sodium Hydroxide.*—Dissolve 50 grams of soda in water, and add water till the solution measures one litre. The solution should be left at rest for a day or two in a stoppered bottle, and then poured off clear into a second bottle. It cannot be filtered.

10. *Solution of Ammonia, or Ammonium Hydroxide.*—Mix 300 c.c. of 'liquor ammoniæ fortior' with 700 c.c. water.

11. *Solution of Calcium Hydroxide, or Lime Water.*—Shake up 10 grams of slaked lime with a litre of water. After about 12 hours the excess of lime will have subsided, and the clear liquid can be drawn off by a siphon. Lime water may be conveniently kept

* c.c. = cubic centimetres.

in a Winchester quart fitted up like a washing bottle (p. 2).

12. *Solution of Sulphuretted Hydrogen.*—Place a litre of water in a clean Winchester quart, and from the apparatus described (pp. 15, 16) pass through it a rapid stream of gas for about ten minutes. Then put the stopper into the bottle and shake up the water thoroughly. Take care the stopper does not get fixed owing to the absorption of the gas. Then repeat the process.

13. *Solution of Ammonium Sulphide.*—This may be purchased. It is easily made thus:—Place any desired quantity of solution of ammonia in a Winchester quart, and pass into it sulphuretted hydrogen gas, until on taking a small quantity of the liquid in a test tube and adding a solution of magnesium sulphate no precipitate is produced.

14. *Solution of Ammonium Carbonate.*—Dissolve in cold water 50 grams of powdered ammonium carbonate, add 100 c.c. solution of ammonia and sufficient water to make the whole measure one litre.

15. *Solution of Ammonium Chloride.*—Dissolve 150 grams of the powdered salt in sufficient water to make a litre.

16. *Solution of Ammonium Oxalate.*—Dissolve 25 grams of the crystals in distilled water, and make up to a litre.

17. *Solution of Ammonium Molybdate.*—Dissolve 50 grams of crystals in a mixture of 100 c.c. of water

and 100 c.c. of solution of ammonia; pour the solution gradually into 500 c.c. dilute nitric acid, shaking constantly, so that the precipitate may be redissolved. Make up with water to 1,000 c.c. Let the solution become quite clear before use.

18. *Solution of Barium Chloride.*—Dissolve 50 grams of the crystals in sufficient water to make up a litre.

19. *Solution of Calcium Sulphate.*—Powder some crystals of gypsum, and then proceed as in making lime water.

20. *Solution of Cobalt Nitrate.*—Dissolve 100 grams of crystals in sufficient water to make a litre.

21. *Solution of Perchloride of Iron.*—Dissolve 10 grams of iron wire in 40 c.c. hydrochloric acid diluted with an equal volume of water. Filter the solution into a large evaporating dish, and add 40 c.c. strong hydrochloric acid and 10 c.c. strong nitric acid, and boil till the somewhat violent reaction is over. Evaporate the liquid till reduced to half its bulk, then dilute to a litre.

22. *Solution of Lead Acetate.*—50 grams of salt dissolved in water, about 10 c.c. acetic acid added, and the whole made up to one litre.

23. *Solution of Magnesium Sulphate.*—50 grams of the salt dissolved in water to make a litre.

24. *Solution of Mercuric Chloride.*—50 grams of the salt dissolved in water sufficient to make a litre.

25. *Solution of Platinum Perchloride.*—Platinum

perchloride is made by dissolving platinum foil in aqua regia, and evaporating the solution to dryness on a water bath. 5 grams of the salt may be dissolved in 100 c.c. of water. As platinum and its compounds are expensive, this solution must be used sparingly, and all liquids containing platinum should be collected in a bottle labelled 'Platinum Residues.' The platinum can be recovered from time to time from these residues as they accumulate. (See Appendix.)

26. *Solution of Potassium Chromate.*—Dissolve 50 grams of the salt in sufficient water to make up a litre.

27. *Solution of Potassium Ferrocyanide.*—20 grams of salt in one litre.

28. *Solution of Potassium Ferricyanide.*—20 grams of salt in one litre.

29. *Solution of Potassium Iodide.*—50 grams of salt in one litre.

30. *Solution of Potassium Theiocyanate.* — 20 grams of salt in one litre.

31. *Solution of Silver Nitrate.*—10 grams dissolved in one litre. Silver solutions and residues should not be thrown away, but should be collected in a large bottle provided for the purpose. The silver can afterwards be recovered and reconverted into nitrate. (See Appendix.)

32. *Solution of Sodium Phosphate.*—50 grams of the salt in one litre.

33. *Solution of Sodium Hydrogen Tartrate.*—80 grams of the salt in one litre. Or the solution may be made by dissolving about 60 grams of tartaric acid

in a litre of water, and dividing the solution into two equal parts. One-half is then heated to boiling and neutralised by Na_2CO_3, added in small quantities till effervescence ceases. The solution of neutral tartrate of sodium thus obtained is then mixed with the remainder of the tartaric acid.

34. *Solution of Tin Protochloride.*—Place in a flask about 25 grams of granulated tin, together with a few scraps of platinum foil and a sufficient quantity of strong hydrochloric acid to cover them. Heat is applied gently till nearly the whole of the tin is dissolved; the solution is then diluted, filtered, and made up by addition of water to a litre. It should be kept in a well-closed bottle in which are placed a few scraps of tin.

35. *Solution of Chlorine or Chlorine Water.*—Chlorine gas is generated by action of hydrochloric acid upon black oxide of manganese, and, after washing through water, the gas is passed into a bottle half full of distilled water. The bottle is closed and shaken up several times in the course of the process, in order to promote the solution of the gas.

Chlorine water must be kept in a dark place or in a bottle covered with thick paper.

36. *Starch.*—A fine white powder insoluble in cold water. Mix one gram of starch with 100 c.c. of water, and heat to boiling. Boil for a few minutes and cool. When required the mucilage must be freshly prepared, as it will not keep.

PART II.

QUALITATIVE ANALYSIS.

TESTS FOR THE CHIEF METALLIC OR POSITIVE SALT RADICLES.

GENERAL DIRECTIONS.

THE student is to perform all the experiments marked A, proceeding in order to the end of the book. This course comprises tests for the following radicles and methods of separation :—

K	Mg	Zn	Hg	As	Ag
Na	Ca	Al	Pb		(Hg_2)
NH_4		Fe	Cu		

in the form of carbonates, sulphites, sulphides, nitrates, chlorides, iodides, acetates, oxalates, tartrates, sulphates, and phosphates. He is then to return and study in the same order the paragraphs marked B.

Tests for the individual members of each analytical group, whether of positive or negative salt radi-

cles must be carefully learnt before proceeding to the consideration of the group as a whole, and before any attempt is made to perform the analysis of a substance of unknown composition.

A short explanation of the mode of applying the reagents is necessary in order to render the whole easily intelligible. Take, for example, the tests first described, namely, those for potassium. Some potassium nitrate (nitre or saltpetre) is to be dissolved in about twenty times its bulk of water.

Test 1. To a portion of this solution, contained in a clean test tube is added some solution of sodium hydrogen tartrate, and the mixture well shaken. A white crystalline precipitate consisting of potassium hydrogen tartrate is slowly thrown down.

Test 2. A second portion of the solution of potassium nitrate is to be mixed in another test tube with a small quantity of hydrochloric acid and solution of platinum perchloride. A yellow crystalline precipitate results.

It is to be understood that the reagents must always be used, unless otherwise distinctly stated, in the form of the solutions for the preparation of which directions have already been given.

In making notes it is a good plan to draw up a table in which the effects of adding the same reagent to the solutions of the different members of the group, (potassium, sodium, and ammonium, for example) are recorded and compared.

Lastly, two or three contractions require explanation. T stands for $C_4H_4O_6$, which represents the negative radicle of a *tartrate.* $\overline{A}$ stands for $C_2H_3O_2$, and indicates an *acetate.* The word *precipitate* is contracted into pp.

Group 1. *K, NH_4, Na.*

A. Chief Tests for **Potassium** in Form of a Salt Dissolved in Water.

Take potassium nitrate, KNO_3.

1. $\overline{N}aH\overline{T}$ (sodium hydrogen tartrate); white crystalline pp. forming slowly ($=KH\overline{T}$).

2. $PtCl_4$ and HCl; yellow crystalline pp. forming slowly ($2KCl.PtCl_4$).

3. Violet flame, often obscured by presence of traces of sodium.

Note. Coloured Flames.—In order to observe the colour communicated to flame by metallic salts and other compounds, the platinum wire (p. 3) is coiled into a flat spiral by winding it about twice round a pencil point. It should not be twisted into a knot, or it will soon break. The wire is then held in the Bunsen flame till the yellow light which it always gives at first has quite disappeared. This yellow colour is due to sodium compounds taken from the fingers. After cleaning it thus in the flame, therefore, the wire must not be touched again, but

dipped at once into the salt or solution to be tested, and the particle thus taken up held in the lower part of the flame. Since sodium compounds, especially common salt, are present almost everywhere in the dust, in common water, in soap, and, as an impurity, in many of the salts to be tested, and since all give a bright yellow light, it must be borne in mind that the mere production of a yellow flame is not proof that the substance for analysis is a compound of sodium. It only becomes proof when it has been shown by proper tests that all other metals are absent. Nevertheless, a little experience will enable the student to distinguish between the transient yellow colour given by small quantities of sodium compounds, present as impurities, and the intense and persistent illumination produced when the substance consists mainly of a salt of sodium. A piece of blue glass may sometimes be used to cut off the yellow rays. The purple flame due to potassium then becomes visible. But since traces of potassium compounds are not unfrequently present as impurity, this plan must not be too much relied upon.

5. Chief Tests for **Ammonium** in Form of a Salt Dissolved in Water.

Take ammonium chloride, NH_4Cl.

1. KHO or NaHO in excess and heated; ammonia (NH_3) evolved. Recognised by smell, by

bluing red litmus paper, and by fuming when brought near a rod wetted with HCl.

2. $NaH\overline{T}$; same as potassium.

3. $PtCl_4 + HCl$; same as potassium.

Dry Test.—Heat some dry ammonium chloride in a test tube. It sublimes. All salts of ammonium are volatile or decomposed by heat. A few, such as phosphate or chromate, leave a residue consisting of the corresponding acid, or a product of its decomposition.

A. Tests for **Sodium** in the Form of a Salt Dissolved in Water.

Take common salt, NaCl.

1. $NaH\overline{T}$ or $H_2\overline{T}$ (tartaric acid); no pp.

2. $PtCl_4 + HCl$; no pp.

3. Flame-coloration yellow.

See *Note* under **Potassium**, p. 43.

A. Detection of the Metals of the First Group when mixed together.

Divide the solution into two parts.

1. Test for NH_4 by adding NaHO to one portion and heating.

2. If NH_4 has not been found, test the second portion for Na and K by taking up a drop of the solution on the platinum wire and holding it in the flame. Then test for K by $NaH\overline{T}$.

If NH_4 has been found, evaporate a fresh portion of liquid to dryness, heat strongly the residue till all fuming ceases, then cool and dissolve in a very little water, and test the solution for K and Na.

Group 2. *Mg, Ba, Sr, Ca.*

A. Chief Tests for **Magnesium** in the Form of a Salt Dissolved in Water.

Take Epsom salt, $MgSO_4.7OH_2$.

1. NH_4HO ; a white pp. (MgH_2O_2) easily soluble in solution of NH_4Cl.

2. KHO or NaHO ; the same.

3. $(NH_4)_2CO_3$; a white pp. ($MgCO_3$), also soluble in NH_4Cl.

4. Na_2HPO_4 ; added to the clear solution obtained by test 1 or 3 gives a white pp.($=MgNH_4PO_4.6OH_2$).

B. Chief Tests for **Barium** in Form of a Soluble Salt Dissolved in Water.

Take barium chloride, $BaCl_2.2OH_2$.

1. $(NH_4)_2CO_3$; white pp. ($=BaCO_3$) insoluble in NH_4Cl.

2. $CaSO_4$ or dilute H_2SO_4 ; immediate white pp. ($=BaSO_4$) insoluble in acids.

3. K_2CrO_4 ; yellow pp. ($=BaCrO_4$) soluble in HCl, but not in $H\overline{A}$.

4. Flame, yellowish green.

B. CHIEF TESTS FOR **Strontium** IN FORM OF A SOLUBLE SALT DISSOLVED IN WATER.

Take strontium nitrate, $Sr(NO_3)_2$.

1. $(NH_4)_2CO_3$; same as Ba.

2. $CaSO_4$ or dilute H_2SO_4; white pp. ($=SrSO_4$), appearing slowly, or after heating.

3. K_2CrO_4; no pp. if $H\bar{A}$ is first added.

4. Flame, crimson, visible through blue glass.

A. CHIEF TESTS FOR **Calcium** IN FORM OF A SOLUBLE SALT DISSOLVED IN WATER.

Take calcium nitrate, $Ca(NO_3)_2$.

1. $(NH_4)_2CO_3$; same as Ba and Sr.

2. $CaSO_4$; no pp.

3. H_2SO_4; crystalline pp. ($=CaSO_4 2OH_2$) unless the solution is very weak.

4. K_2CrO_4; no pp.

5. Flame, orange red, or, when seen through blue glass, dingy green.

6. $(NH_4)_2C_2O_4$ (oxalate) may often be used as a confirmatory test, especially for detecting Ca in presence of Mg, K, NH_4, or Na. It gives a white pp. ($=CaC_2O_4$). Salts of Ba and Sr give pps. of same appearance, which are rather more soluble in $H\bar{A}$ than CaC_2O_4.

A. Separation of Calcium from Magnesium.—Add to the solution an equal volume of solution of

NH_4Cl, then a little NH_4HO, and finally $(NH_4)_2CO_3$ as long as a precipitate is formed. Filter.

Precip. = $CaCO_3$. Re-dissolve in acetic acid and confirm by flame test and by $(NH_4)_2C_2O_4$, which gives a white pp. of CaC_2O_4.

Filtrate.—Add Na_2HPO_4; a white pp. is formed, $MgNH_4PO_4.6OH_2$.

A. Separation of Calcium, Magnesium, Potassium, Sodium, and Ammonium.—Add NH_4Cl, then NH_4HO and $(NH_4)_2CO_3$, and warm gently. Filter.

Precip. = $CaCO_3$. Re-dissolve off the filter in $H\bar{A}$ and confirm by $(NH_4)_2C_2O_4$.

Filtrate.—Divide into two parts.

1. Test for Mg by Na_2HPO_4.
2. Test for K and Na by p. 45.

Test for NH_4 in a portion of the original solution.

B. Detection of the Members of the Second Group when mixed together.—The solution must not contain free HCl or HNO_3; if it does, add excess of NH_4HO. Add a little $H\bar{A}$, then K_2CrO_4 till the liquid is pale yellow.

Yellow pp. = $BaCrO_4$.

Filter off the pp. and divide the liquid into two parts.

a. Test for Sr by boiling with $CaSO_4$.

b. If Sr is not found, test for Ca by $(NH_4)_2C_2O_4$ (oxalate), which will give a white pp.

If Sr is found, add *slight* excess of dilute H_2SO_4; boil, filter, and test for Ca by $(NH_4)_2C_2O_4$.

Confirm by spectroscope (see note).

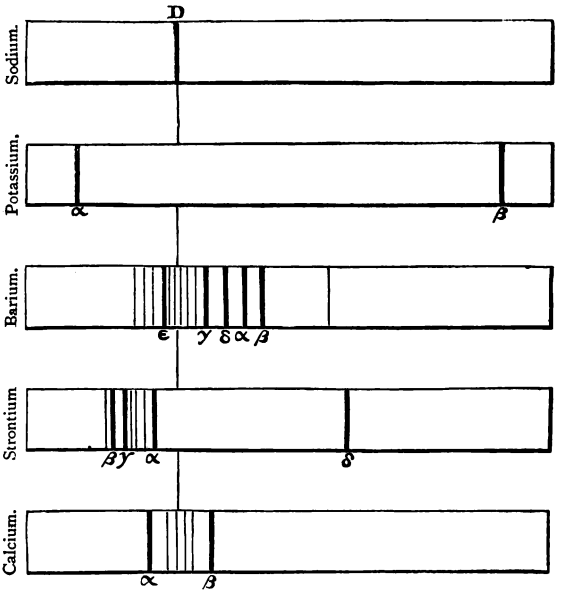
Note. Use of the Spectroscope.—The detection and recognition of the metals potassium and sodium, barium, strontium and calcium, are easily accomplished, even in presence of one another, by the use of the spectroscope. The most convenient instrument for laboratory use is a small pocket direct-vision spectroscope, such as may be purchased from the chief instrument makers for a comparatively small sum. With this instrument the whole spectrum is seen at once.

Draw out the eye-piece till, on looking through at the window, the spectrum is seen clearly, then contract the slit at the opposite end till the black lines of sunlight are visible. Or direct the instrument to a flame coloured by sodium, and arrange the slit so that the yellow line, then visible, may be very thin. The spectroscope will now be ready to use. Take up a particle of the salt to be tested on a clean platinum wire, hold it in the Bunsen flame, and look at the flame through the spectroscope. In place of the continuous spectrum previously seen, a number of brilliant coloured lines will be apparent, separated by dark intervals. The colour, number, position, and relative intensities of these lines will depend upon the nature of the substance. For beginners it is sufficient to learn the following five spectra, in which the relative positions and intensities of the

lines are indicated by the diagram. The brightest line is marked α, the rest β, γ, δ, &c., in order.

The spectrum of sodium, as seen in the small spectroscope, consists of a single yellow line, and,

FIG. 6.



owing to the general diffusion of sodium already referred to (p. 44), this yellow line is almost always perceived simultaneously with the spectra of the other metals. The violet line, β, of potassium is not easily seen, but the red line is very characteristic. In the

case of a mixture it must not, however, be confounded with the red strontium line, which is much nearer to the yellow. Strontium is always very easily recognised by the aid of the isolated blue line, δ.

Group 3. *Zn, Mn, Ni, Co.*

A. Chief Tests for Zinc in the Form of a Soluble Salt Dissolved in Water.

Take zinc sulphate, $ZnSO_4.7OH_2$.

1. KHO, NaHO, or NH_4HO; a white pp. (ZnH_2O_2) easily soluble in excess.

2. Add NH_4Cl to the solution obtained by test 1; no pp. Compare Al.

3. Add H_2S to the same solution; white pp.= ZnS. NH_4HS produces the same pp. with all solutions of zinc.

Blowpipe.—Heat some of the dry salt on charcoal; a yellow mass remains, which becomes white on cooling (=ZnO). Wet it with a drop of $Co(NO_3)_2$, and heat again; it becomes green.

A. Separation of Zinc from Calcium, Magnesium, &c.—Add to the liquid some solution of NH_4Cl, then excess of NH_4HO, and lastly NH_4HS.

Precip. 1.—White = ZnS. Collect on a filter, wash, and dry the pp. Confirm by heating on charcoal, first alone, and then with $Co(NO_3)_2$.

Filtrate.—Add $(NH_4)_2CO_3$.

(See next page.)

Precip. 2. $=CaCO_3$. Filter, and test the filtrate for Mg, K, Na.

Test for NH_4 in the original solution.

B. CHIEF TESTS FOR **Manganese** IN THE FORM OF A SOLUBLE SALT DISSOLVED IN WATER.

Take manganese chloride, $MnCl_2.4OH_2$.

1. Note that the solution is pale pink.

2. KHO or NaHO; a white pp. (MnH_2O_2), becoming brown on exposure to air.

3. NH_4HO; same pp. Its formation is prevented for a time by first adding NH_4Cl.

4. NH_4HS; pink pp. (MnS), becoming brown.

Blowpipe.—Make a bead of KNO_3 on a loop of platinum wire, and fuse with a *very small* particle of any manganese compound. A deep-green mass remains (K_2MnO_4, manganate).

B. CHIEF TESTS FOR **Nickel** IN THE FORM OF A SOLUBLE SALT DISSOLVED IN WATER.

Take nickel sulphate, $NiSO_4.7OH_2$.

1. Note that the solution is green.

2. KHO or NaHO; pale green pp. (NiH_2O_2).

3. NH_4HO; the same, easily soluble in excess, forming a blue liquid.

4. NH_4HS; a black pp. (=NiS). If yellow $(NH_4)_2S_2$ is used the pp. is slightly soluble in excess, giving a nearly black liquid.

B. CHIEF TESTS FOR **Cobalt** IN THE FORM OF A SOLUBLE COBALTOUS SALT DISSOLVED IN WATER.

Take cobalt nitrate, $Co(NO_3)_2.6OH_2$.

1. Note that the solution is pale red.

2. KHO or NaHO ; a blue pp. (CoH_2O_2), which becomes brown on boiling.

3. NH_4HO ; bluish-green pp., not formed in presence of NH_4Cl.

4. NH_4HS ; black pp. (CoS), not soluble in yellow ammonium sulphide.

Blowpipe.—Borax bead on platinum wire moistened with the solution and fused again becomes blue.

B. Detection of the Metals of the Third Group when mixed together.—Add to the solution, which should be slightly acid, some sodium acetate, and, if strong, dilute with water and pass a rapid stream of H_2S. Sulphides of zinc, cobalt, and nickel, being insoluble in acetic acid, are precipitated. Filter. Add to the filtrate a little more solution of sodium acetate, and pass H_2S again, to ensure the complete precipitation of the three sulphides. If there is no further pp., proceed.

Test the filtrate for Mn by adding NH_4HO and NH_4HS. Pink pp.=MnS.

If the first pp. was white it contains ZnS only.

If black, boil in small quantity of HCl with a few drops of HNO_3, till dissolved. Add excess of NaHO, and filter.

Filtrate.—Add NH_4HS ; white pp.=ZnS.

Precipitate.—Test for Co by borax bead. If Co is not found, test for Ni by redissolving the pp. in HCl, adding NH_4HO and excess of yellow ammonium sulphide. A black liquid indicates nickel.

If Co is present dissolve the pp. in the least possible quantity of aqua regia. Add NaHO till the pp. locally formed is only just re-dissolved, so that the liquid is left only slightly acid ; then add very little solution of *pure* KCN, so as just to re-dissolve the pp. which addition of the first few drops produces. Pour into a small flask or beaker, place it over a lamp *in the fume closet*, and boil for about five minutes. When cold, add solution of sodium hypochlorite, or excess of bromine water, and some solution of soda, and warm *gently* ; a black pp. of $Ni_2(HO)_6$ is formed sooner or later if Ni is present. This precipitate, containing Ni, should be filtered off, washed with hot water, and tested with a borax bead to show that it is free from Co.

Group 4. *Al, Fe, Cr.*

A. Chief Tests for **Aluminium** in the Form of a Soluble Salt Dissolved in Water.

Take common alum, $(NH_4)_2SO_4.Al_2(SO_4)_3.24OH_2$.

1. NH_4HO ; a white translucent pp. $(Al_2H_6O_6)$,

almost insoluble in excess of NH_4HO, insoluble in NH_4Cl. Compare Mg and Zn.

2. KHO ; same pp., but easily soluble in excess. Compare Mg and Zn.

3. Add excess of NH_4Cl to the clear liquid obtained by test 2 and heat it. $Al_2(HO)_6$ is thrown down again. Compare Zn.

4. Take up a crystal of alum on a platinum loop, heat it in the Bunsen flame. It melts, then swells up, and gives off water. Finally heat the mass as strongly as possible in the blowpipe flame, and observe that it glows brightly but is infusible (Al_2O_3). Moisten this with $Co(NO_3)_2$ and heat again. On cooling, the mass will be found to be bright blue.

A. Chief Tests for Iron in The Form of a Soluble **Ferrous** Salt Dissolved in Water or Dilute Acid.

Take ferrous sulphate, $FeSO_4.7OH_2$.

1. Note that the solution is pale green.

2. NaHO, KHO, or NH_4HO ; a white pp. (FeH_2O_2), becoming immediately green, and finally brown, from oxidation.

3. $K_4FeC_6N_6$ (ferrocyanide) ; a pale blue pp.

4. $K_6Fe_2C_{12}N_{12}$ (ferricyanide) ; dark 'Turnbull's' blue.

5. KCNS ; no change if the solution is free from ferric salt.

6. Boil with a few drops of strong HNO_3. The liquid becomes black, effervesces, and then turns yellow. It now contains *ferric* salt.

A. Chief Tests for Iron in the Form of a Soluble **Ferric** Salt Dissolved in Water or Dilute Acid.

Take the solution obtained by test 6, above.

1. Note that the solution is yellow.

2. NaHO, KHO, or NH_4HO; a brown pp. ($Fe_2H_6O_6$).

3. $K_4FeC_6N_6$; a deep blue pp.='Prussian blue.'

4. $K_6Fe_2C_{12}N_{12}$; no pp., but deep greenish or brown colour.

5. KCNS; deep red colour.

6. Both ferrous and ferric solutions give with NH_4HS a black pp. (=FeS).

A. Separation of Iron from Aluminium.—Dilute a portion of the solution and add ferricyanide of potassium. If the presence of any ferrous salt is indicated, it must be converted into ferric salt before proceeding. This is done by boiling a fresh portion of the solution with a few drops of nitric acid.

Then add NaHO in excess. Warm gently and filter.

Precip.—Brown = $Fe_2(HO)_6$. Confirm by re-dissolving in HCl and adding ferrocyanide.	*Filtrate.*—Add NH_4Cl and heat. White pp. = $Al_2(HO)_6$.

A. Separation of Zinc from Iron and Aluminium.—Boil with a few drops of HNO_3, if necessary, to convert all ferrous into ferric salts, then add NH_4HO in excess. Filter.

Precip.—
If white = $Al_2(HO)_6$.
If brown, contains $Fe_2(HO)_6$, and perhaps $Al_2(HO)_6$. Dissolve in dilute HCl, and add NaHO in excess. The iron is precipitated, the aluminium left in solution, as in the directions already given for separating iron from aluminium.

Filtrate.—Add NH_4HS or H_2S; white pp. = ZnS.

A. Separation of Zinc, Iron, and Aluminium from Calcium, Magnesium, Potassium, Sodium, and Ammonium.—Boil with nitric acid and add excess of NH_4Cl and NH_4HO, and filter.

Precip. 1 = $Fe_2(HO)_6$ and $Al_2(HO)_6$. Wash, re-dissolve off the filter in dil. HCl; separate the iron from the aluminium by soda (see p. 56).

Filtrate 1.—Add NH_4HS in excess and filter. See 2, below.

Precip. 2. = ZnS.

Filtrate 2. — Add $(NH_4)_2CO_3$, and filter.

Precip. 3. = $CaCO_3$.

Filtrate 3. — Finish by p. 48.

B. CHIEF TESTS FOR **Chromium** IN THE FORM OF A SOLUBLE SALT DISSOLVED IN WATER.

Take chrome alum, $K_2SO_4.Cr_2(SO_4)_3.24OH_2$.

1. Note that the salt is dark purple, but yields a green solution in boiling water.

2. NH_4HO ; a dull green pp. ($Cr_2H_6O_6$), slightly soluble in great excess of NH_4HO, forming a reddish liquid.

3. KHO or NaHO ; the same pp., soluble in excess of the alkali, forming a green solution.

Blowpipe Test.—Fuse some of the dry salt with a bead of nitre upon a loop of platinum wire. A yellow mass of chromate is formed. This mass is soluble in water, and the solution answers to the tests given on p. 93.

B. Detection of the Metals of the Fourth Group when mixed together.

1. Test a separate portion of the liquid for ferrous salt. If this is present, boil the portion which is to be further tested with nitric acid.

2. Add excess of NH_4HO and collect the pp. If quite white it consists only of $Al_2(HO)_6$; if green it may consist of $Cr_2(HO)_6$, alone or mixed with $Al_2(HO)_6$; if brown it may contain all three. Drain and dry it. Mix the dry powder with Na_2CO_3 and a little KNO_3, and melt at a red heat in a pla-

tinum capsule for five minutes. Cool, boil in water, and filter.

Residue=Fe_2O_3, brown.

Filtrate.—If yellow, Cr is present. Divide into two parts: (*a*) add NH_4Cl and heat: white pp.=$Al_2(HO)_6$; (*b*) add $\overline{HA}$ and excess of $AgNO_3$: red pp. = Ag_2CrO_4.

3. If ferrous salt was not present in the original, a brown insoluble residue after fusion indicates ferric salt. Confirm by testing the original solution with $K_4FeC_6N_6$ and KCNS.

Group 5a. Hg, Pb, Bi, Cu, Cd.

A. Chief Tests for Mercury in the Form of a Soluble Mercuric Salt Dissolved in Water.

Take corrosive sublimate, $HgCl_2$.

1. H_2S, added gradually, gives a white pp., which then becomes brown and finally black (=HgS).

2. $SnCl_2$; a white pp. (=Hg_2Cl_2), which becomes black by heating with excess of $SnCl_2$ (=Hg).

3. KI; a scarlet pp. (=HgI_2), easily soluble in excess of $HgCl_2$ or of KI.

4. Copper foil heated gently in the liquid, slightly acidified with HCl, becomes coated with a shining white film of mercury. If a grey coating is formed it will become bright on rubbing.

Dry Tests.

1. Heat some calomel, Hg_2Cl_2, in a small dry test tube; it sublimes.

All mercurial compounds, when heated, vaporise, and many yield a sublimate of mercury, owing to decomposition. Thus mercuric oxide splits up into mercury and oxygen. Mercury nitrates evolve nitric peroxide, N_2O_4, and leave red mercuric oxide, which in its turn volatilises if the application of heat is continued. Mercury phosphates leave a residue of metaphosphoric acid. Mercury chromates yield green oxide of chromium (Cr_2O_3).

2. Heat some calomel with dry Na_2CO_3 in a narrow tube. A grey sublimate of metallic mercury forms upon the cool part of the tube.

All mercurial compounds behave in the same way.

A. Chief Tests for **Lead** in the Form of Soluble Salt Dissolved in Water.

Take lead nitrate, $Pb(NO_3)_2$.

1. H_2S in excess; black pp. (=PbS).

2. HCl; white crystalline pp. (=$PbCl_2$), unless the solution is very weak. $PbCl_2$ dissolves readily in hot water and crystallises on cooling.

3. Dilute H_2SO_4, added in considerable quantity; white pp. (=$PbSO_4$).

4. KI; golden yellow pp. ($=PbI_2$), soluble in boiling water and crystallising on cooling.

Blowpipe.—Heat with some Na_2CO_3 and KCN on charcoal. Globules of lead are formed, which mark paper and are easily flattened by pressure.

A. CHIEF TESTS FOR COPPER IN THE FORM OF A **Cupric** SALT DISSOLVED IN WATER.

Take copper sulphate, $CuSO_4.5OH_2$.

1. Note that the solution is blue.

2. H_2S; black pp. (CuS), insoluble in dilute acids and in NaHO, very slightly soluble in yellow ammon. sulphide.

3. NH_4HO added gradually; a greenish pp., easily soluble in excess, giving a deep blue liquid.

4. $K_4FeC_6N_6$, ferrocyanide; a reddish brown pp. ($Cu_2FeC_6N_6$).

5. After addition of a few drops of acid, a clean piece of iron (e.g. a knife-blade) dipped into the solution becomes coated with copper.

A. Detection of Mercury, Lead, and Copper in the presence of one another.

Add dilute H_2SO_4 in excess. Filter.

Precip. — White = $PbSO_4$. Confirm by drying it and reducing with KCN on charcoal.

Filtrate.—Divide into two parts.

1. Test for Hg by $SnCl_2$ or by copper.

2. Test for Cu by excess of NH_4HO, or by ferrocyanide.

If Hg is present a white pp. ($HgNH_2Cl$) will be thrown down by ammonia; but this will not prevent the blue colour of the liquid from being seen.

B. CHIEF TESTS FOR **Bismuth** IN THE FORM OF NITRATE OR CHLORIDE DISSOLVED IN DILUTE HNO_3 OR HCl.

1. H_2S; black pp. ($=Bi_2S_3$). Compare Sb.

2. *Water* added in considerable quantity gives with the chloride a white pp. ($=BiOCl$).

If the nitrate has been used, add some NH_4Cl before the water. This pp. is not dissolved by tartaric acid. Compare Sb.

Blowpipe.—Heat some dry bismuth salt (say, $BiONO_3$) with Na_2CO_3 and KCN on charcoal. Very brittle white globules of bismuth are formed.

B. CHIEF TESTS FOR **Cadmium** IN THE FORM OF A SOLUBLE SALT DISSOLVED IN WATER.

Take cadmium sulphate, $CdSO_4.5OH_2$.

1. H_2S; bright yellow pp. (CdS). This pp. is insoluble in—

a. $(NH_4)_2S$.

b. NaHO or KHO.

c. Solution of KCN.

But is soluble in—

a. Boiling strong HCl.

b. Boiling dilute H_2SO_4.

Compare As and Cu.

2. NH_4HO; white pp., very easily soluble in excess.

B. Detection of the Metals of the Fifth (*a*) Group when mixed together.—Add a little HCl, then saturate the liquid with H_2S, and filter off the pp. Wash it well and boil with a little strong HNO_3. Evaporate away most of the acid; then add a little dilute sulphuric acid and some water, and filter.

Insoluble Residue.—If white, consists only of $PbSO_4$ (partly produced by oxidation of PbS). Boil with solution of ammonium acetate, which dissolves it; then test for lead by adding K_2CrO_4. Or better, dry the powder and reduce on charcoal.

If black, may contain HgS and $PbSO_4$. Boil with $NH_4C_2H_3O_2$ and filter. Test the solution for Pb by K_2CrO_4, and the black residue for Hg by dissolving in a few drops of aqua regia, diluting with water and testing with copper or $SnCl_2$.

Filtrate from insoluble residue.—Add excess of NH_4HO, and filter.

Precip.—$Bi(HO)_3$. Wash, then dissolve in the least quantity of HCl, and add much water; white milkiness = Bi.

Filtrate.—If quite colourless test for Cd by adding H_2S.

If blue, copper is present. Add solution of KCN till decolorised, then a small quantity of H_2S. A yellow precipitate consists of cadmium sulphide, CdS.

Group 5b. As, Sb, Sn.

A. CHIEF TESTS FOR ARSENIC IN THE FORM OF **Arsenious Anhydride** (As_2O_3).

1. Heavy white lumps or powder. Heated gently in a dry test tube, sublimes completely, giving a glittering deposit of minute octahedral crystals. Examine these carefully under a lens or microscope.

2. The powder mixed with dry powdered KCN, and heated in a narrow test tube, gives a shining black sublimate of elemental arsenic.

A. CHIEF TESTS FOR ARSENIC IN THE FORM OF AN **Arsenious** COMPOUND IN SOLUTION.

Take solution obtained by boiling white arsenic (As_2O_3) in water for some time.

1. H_2S ; a yellow solution. If HCl is added, either before or after the H_2S, a yellow pp. (As_2S_3), which is insoluble in boiling strong HCl, but dissolves readily in yellow ammonium sulphide or in potash or soda.

2. $AgNO_3$; a yellow pp. (Ag_3AsO_3), soluble in nitric acid or in solution of ammonium hydrate.

3. *Reinsch's Test.*—The liquid is acidified with HCl and a piece of bright copper foil heated in it. The copper becomes coated with a grey crust (As_2Cu_5). It must be taken out, dried, and heated strongly in a small test-tube. A sublimate of crystals (As_2O_3) is formed.

A. Separation of Arsenic from Mercury, Lead, and Copper.—Acidify the solution, if necessary, with HCl and saturate with H_2S. Filter off the pp., wash with water, and boil with $(NH_4)_2S_2$.* Add water and filter.

Solution.—Add HCl in excess. A yellow pp. $=As_2S_3$. A slight white pp. of sulphur may be neglected.

Residue on filter consists of HgS, PbS, CuS. If these are to be identified, dissolve the pp. in the least possible quantity of HCl and HNO_3 by boiling, and test for the lead by dilute H_2SO_4, for the Hg by copper, and for the copper by ammonia, as on p. 61.

A. Separation of Arsenic, Mercury, Lead, and Copper from Zinc, Iron, Aluminium, Calcium, Magnesium, &c.—Acidify the solution with HCl, and saturate with H_2S.

Precipitate.—As_2S_3, HgS, PbS, CuS, to be dealt with as above by boiling with $(NH_4)_2S_2$, &c.

Solution filtered off contains all the rest. Boil it first alone, to expel H_2S; then with a little HNO_3, to convert ferrous into ferric salts, if present. Then add NH_4Cl † and NH_4HO in excess.

* If the original liquid was blue, owing to the presence of copper, NaHO may be used instead of $(NH_4)_2S_2$.

† To prevent partial precipitation of Mg, if present in quantity.

Precipitate.—$Al_2(HO)_6$ and $Fe_2(HO)_6$; filter if necessary, and add to the solution NH_4HS.

White pp.=ZnS.

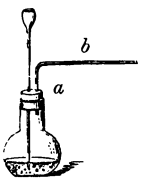
Filter if necessary, and add $(NH_4)_2CO_3$ and heat.

White pp.=$CaCO_3$.

Filter if necessary, and test the solution for Mg, K, Na, as on p. 48.

B. Marsh's Test for Arsenic.—A small flask, arranged as in the figure, is required. To the tube *a* is fitted by an india-rubber joint a piece of hard glass tubing *b* drawn out to a point.

FIG. 7.



Some granulated zinc is put into the flask with a little water, and enough hydrochloric acid added to start a brisk effervescence. As soon as the air is all expelled,* the escaping jet of hydrogen is ignited, and then a *small quantity* of the solution of arsenic added through the funnel. Arsenetted hydrogen, AsH_3, now accompanies the hydrogen. *Remember that the gas and the fumes produced by its combustion are very poisonous, and therefore avoid inhaling them.* The experiment ought to be made in a draught cupboard or in the open air.

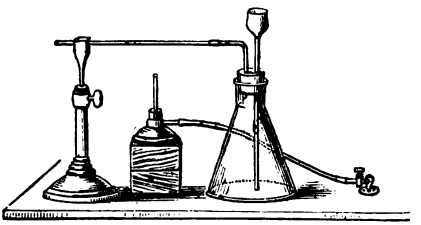
A white china plate held in the flame becomes coated with a brown or black metallic stain of As. The

* Which is ascertained by collecting some of the hydrogen in a test tube and lighting it. It should burn quietly.

spots are immediately dissolved by solution of chlorinated soda ($NaClO + NaCl$). Compare Sb.

Another Way of Testing the Gas for As.—Support the escape tube by the ring of a retort stand or otherwise, and apply a Bunsen flame near the middle till the glass is almost red hot. A mirror-like deposit of arsenic will be formed inside the tube just beyond the flame. If the tube is afterwards cut off here, the stain will be found to be soluble in chlorinated soda; or if the piece of tube, now open at both ends, is held in a

FIG. 8.



slanting position over a flame, so that the mirror alone is heated, it will give a sublimate of crystals (1, p. 64).

B. Hofmann's Test for Arsenic.—By means of the apparatus employed for Marsh's test generate AsH_3; but instead of burning the gas conduct it, by means of a bent piece of tubing, into a test tube containing solution of silver nitrate. A black pp. of metallic silver is formed, whilst nitric acid and arsenious acid remain in solution. After the gas

has been passing for about five minutes filter the liquid in the tube, add a little more silver nitrate, and then very cautiously a few drops of solution of ammonia, to neutralise the nitric acid. A yellow pp. of Ag_3AsO_3 is formed.

B. Fleitmann's Test for Arsenic.—Boil a piece of granulated pure zinc or aluminium foil with solution of soda; hydrogen is evolved. Add a few drops of solution of As_2O_3; the escaping gas now contains AsH_3, which may be recognised by its blackening a piece of filter paper wetted with $AgNO_3$ and held over the mouth of the test tube. This stain disappears on wetting it with diluted HNO_3, whereby it is proved not to consist of Ag_2S. This test is useful for distinguishing readily As from Sb, the compounds of which are not reduced to SbH_3 in alkaline solution.

B. CHIEF TESTS FOR ANTIMONY IN THE FORM OF **Antimonious** CHLORIDE DISSOLVED IN DILUTE HCl.

1. Water; a white milkiness, due to precipitation of SbOCl. This pp. is easily soluble in warm hydrochloric or tartaric acid. Compare Bi.

2. H_2S; an orange pp. (Sb_2S_3), soluble in hot HCl (compare As), also soluble in $(NH_4)_2S_2$ and in NaHO or KHO.

Blowpipe Test.—A dry compound of antimony

(e.g. Sb_2O_3, or 'tartar emetic') heated with KCN on charcoal gives very brittle globules of metal, with a white smoke of oxide upon the charcoal.

B. Marsh's Test for Antimony.—Take the same apparatus as for detection of arsenic, using fresh zinc. Add a few drops of the acid solution of $SbCl_3$, and burn the gas as before. The stains formed upon the porcelain are less lustrous than arsenic stains, and are not soluble in the solution of chlorinated soda.

B. Hofmann's Test for Antimony.—Proceed as in testing for arsenic. A black pp. will be formed in the solution of silver nitrate, but this contains the antimony in form of $SbAg_3$, whilst nitric acid remains in solution.

Collect the pp. and wash it well upon a filter; then boil it with solution of $NaH\bar{T}$, to extract the antimony; add a few drops of HCl; filter, if necessary, and test for Sb by H_2S.

B. Chief Tests for Tin in Form of **Stannous Chloride** Dissolved in Hydrochloric Acid.

1. H_2S; dark brown pp. (SnS), soluble in hot solution of KHO, and, on addition of excess of HCl, reprecipitated unchanged. Also soluble in yellow ammonium sulphide. On adding HCl to this liquid a yellow pp. of SnS_2 is formed.

2. $HgCl_2$; white pp. (Hg_2Cl_2), which if boiled with excess of stannous chloride becomes black, Hg.

B. Tests for Tin in Form of **Stannic Chloride** Dissolved in Hydrochloric Acid.

1. H_2S ; dull yellow pp. (SnS_2), difficult to filter off till it has been well boiled. Soluble in KHO or in Am_2S_2, and reprecipitated unchanged by acid.

2. $HgCl_2$; no pp.

B. Tests for **Tin** as Stannous or Stannic Compound.

1. Zinc added to an acid solution becomes covered with crystals of metallic tin. All the tin is ultimately thrown down. Tin is soluble in boiling hydrochloric acid, and the solution contains $SnCl_2$.

2. *Blowpipe.*—A dry tin compound heated with KCN on charcoal gives white globules of metal, which are malleable, but do not mark paper.

B. Separation of the Metals of the Fifth (*b*) Group when mixed together.—Either of the following processes may be used :—

I. Precipitate the three metals in form of sulphides by adding HCl and excess of H_2S. Collect the pp., drain it well, and boil in a test tube with strong HCl ; add a little water, and filter.

Insoluble Residue.—Yellow As_2S_3. Wash with hot water acidified with HCl, then with water, and dry in water bath. Heat a portion with KCN in a tube (2, p. 64).

Solution.—Test for Sb by Marsh's test, following directions given, p. 69.

After the action has gone on for some time, and nearly all the zinc is dissolved, pour away the solution. The tin will then be found in the black residue. Boil it with a little strong HCl till dissolved, then test the solution with $HgCl_2$.

II. *Hofmann's Method.*—Pour the solution into the flask containing zinc, and pass the gas into solution of silver nitrate. The black pp. must be filtered off, washed well, and tested for Sb. The remaining solution is neutralised with NH_4HO (see p. 68).

The tin is found in the generating flask, and is tested for as in process I.

Group 6. *Ag, Hg, Pb.*

A. Chief Tests for **Silver** in the Form of a Soluble Salt Dissolved in Water.

Take silver nitrate, $AgNO_3$.

1. HCl ; a white pp. (AgCl), which, unless too much HCl has been added, easily separates from the liquid in clots or lumps. The pp. becomes purplish when exposed to sun light ; it is very soluble in NH_4HO, but not in strong HNO_3.

2. Solution of KCN ; a white curdy pp., resembling the chloride, very easily soluble in excess of KCN. The solution rubbed upon clean copper produces a white stain of silver, which is not driven away by heat.

A. CHIEF TESTS FOR MERCURY IN THE FORM OF A **Mercurous** SALT DISSOLVED IN WATER.

Take solution of $Hg_2(NO_3)_2$ in dilute HNO_3.

1. Mercurous salts are volatilisable by heat, and in general behave in the same way as mercuric salts. The most important difference is in the action of—

2. HCl; a white pp. (Hg_2Cl_2), converted by heating with HNO_3, or aqua regia, into soluble mercuric salts.

NH_4HO changes it into black insoluble Hg_2NH_2Cl.

A. The tests for **Lead** are given on p. 60.

When the solution is weak no pp. is produced by HCl in solution of a lead salt.

A. Separation of the Metals of the Sixth Group when mixed together.—Add HCl as long as any pp. is thrown down, and filter. Remember that if any lead is present, a part of it will remain in solution.

Boil the pp. with water, and filter.

Filtrate.—Set it by and observe whether crystals of $PbCl_2$ are deposited. If not, add excess of dilute H_2SO_4, and look for white pp. of $PbSO_4$.

Insoluble Portion of Precipitate on the Filter.—Pour over it some NH_4HO, and collect liquid in a clean test tube. Add excess of HNO_3 to the clear liquid; a white curdy pp. = AgCl. A black residue on the filter indicates Hg.

B. *Notes.*—1. It sometimes happens that a white pp., SbOCl or BiOCl, makes its appearance when the solution contains antimony or bismuth. This is not to be confounded with the silver group; it re-dissolves immediately when a sufficient quantity of HCl is added.

2. If the solution contained nitric acid the addition of hydrochloric acid would decompose mercurous nitrate, if present; but the pp., Hg_2Cl_2, will re-dissolve if the liquid is boiled, being converted into mercuric chloride.

3. Sulphur is thrown down by HCl in the form of a white precipitate if the liquid contains an alkaline polysulphide, or as a pale yellow precipitate if it contains a theiosulphate. Such salts, however, are not likely to accompany Ag, Pb, or Hg.

A. Separation of Silver, Lead, and Mercury (as Mercurous Salt) from the rest of the Metals.—Add hydrochloric acid as long as a pp. is thrown down.

Precipitate.—AgCl, Hg_2Cl_2, and $PbCl_2$. These may be dealt with as on preceding page.

Filter.

The filtrate contains all the other metals, because their chlorides are soluble in water. Test by directions on p. 65.

The table on the opposite page gives a synopsis of the whole process. Before commencing, read through carefully the general directions given on page 75.

REVIEW OF THE ANALYTICAL GROUPING OF THE METALS.

Group VI.	Group V.		Group IV.	Group III.	Group II.		Group I.
	A.	B.			A.	B.	
Ag	Pb	As	Fe	Zn	Ba	Mg	K
Hg(ous)	Hg(ic)	Sb	Al	Mn	Sr.		Na
Pb	Bi	Sn	Cr	Ni	Ca		NH_4
	Cu			Co			
	Cd						

VI. Thrown down as insoluble (ex. Pb) chlorides —AgCl, Hg_2Cl_2, and $PbCl_2$,—all other chlorides being easily soluble in dilute HCl.

V. Thrown down by H_2S as sulphides from a solution acidified with HCl, the sulphides of the succeeding groups being soluble in dilute HCl. This group admits of two subdivisions.

A. Sulphides—PbS, HgS, Bi_2S_3, CuS, CdS—insoluble in $(NH_4)_2S_2$ or NaHO.

B. Sulphides—As_2S_3, Sb_2S_3, SnS, and SnS_2—soluble in $(NH_4)_2S_2$ or NaHO.

IV. After removing the two preceding groups the addition of NH_4HO under proper conditions throws down $Fe_2(HO)_6$, $Al_2(HO)_6$, and $Cr_2(HO)_6$, with small quantities of $Mn_2(HO)_6$ when Mn is present.

III. After removing the three preceding groups these are the only metals which form sulphides

insoluble in water or alkaline solutions :—ZnS, MnS, CoS, NiS. These sulphides are not formed in presence of HCl.

II. Alkaline earth metals. Sulphides soluble in acids and more or less in water, and therefore cannot be precipitated. The group is divided into two parts.

A. Carbonates—$BaCO_3$, $SrCO_3$, $CaCO_3$—insoluble in NH_4Cl.

B. Carbonate—$MgCO_3$—soluble in NH_4Cl.

I. Alkali metals. Sulphides, carbonates, hydroxides, phosphates, all soluble in water.

TABLES OF SHORT DIRECTIONS FOR THE DETECTION OF ANY OF THE COMMON METALS IN AN AQUEOUS OR SLIGHTLY ACID SOLUTION.

These tables include and reproduce the directions for the separation of the groups as already given.

In adding the reagents, if the addition of a small quantity fails to produce a precipitate, the group is probably absent. But if a precipitate forms, be sure to add sufficient of the reagent to throw down the whole of that group. It is necessary to use especial care to ensure excess of sulphuretted hydrogen.

Take care that after addition of each reagent liquids are well mixed.

If oxidising agents are present (such as c

nitrous acid, or sulphurous acid) H_2S will often give a pp. of sulphur. If this happens, boil the liquid well for a few minutes before passing in the gas. If there is much nitric acid it should be evaporated away, and the liquid diluted with water.

Wash every precipitate once or twice by pouring hot water over the filter containing it.

When the quantity of precipitate to be treated with acid is considerable, it may be taken off the filter by help of a slip of glass or wood, or a platinum spatula, and placed in the test tube in which it is to be boiled. But when the precipitate is very small it is best to wash it well, tear off that part of the filter which contains nothing, and place the rest, with the precipitate adhering to it, in a test tube with a small quantity of the solvent. Boil it, if necessary, then add some water, and filter from the undissolved pulp.

CHARACTERS OF THE CHIEF NEGATIVE SALT RADICLES, AND TESTS.

FIRST DIVISION.

Salts which, when gently heated with dilute sulphuric acid, evolve gas or vapour.

Carbonates	evolve	CO_2
Sulphites	„	SO_2
Theiosulphates	„	SO_2

Sulphides	„	H_2S
Hypochlorites	„	Cl_2
Nitrites	„	N_2O_3
Cyanides	„	HCN
Ferrocyanides	„	HCN } see Second
Ferricyanides	„	HCN } Division.

A. Carbonates.

Examples of Common Carbonates:—

Smelling salts, $(NH_4)_2CO_3$.*
Washing soda, $Na_2CO_3.10OH_2$.
Chalk or marble, $CaCO_3$.
Magnesia, $MgCO_3$.†

1. All carbonates are insoluble in water except carbonates of K, Na, NH_4.

2. All carbonates evolve CO_2 when heated to redness, except K_2CO_3, Na_2CO_3.

3. All carbonates effervesce on the addition of an acid; the escaping gas (CO_2) is without smell.

Take some Na_2CO_3 in a test tube and pour on a little dilute H_2SO_4. Test for the presence of CO_2 by dipping a clean quill tube into clear lime water and holding it in the gas. The drop becomes milky.

* Really a mixture of two or more ammonium compounds, of which this is perhaps the chief.

† True formula, $3MgCO_3 + Mg(HO)_2 + 4OH_2$. Nearly all carbonates, except those of the alkalies and alkaline earths, contain hydroxide.

B. Hydric Carbonates.—The only definite compounds of this kind are the 'bicarbonates' of potassium, sodium, and ammonium. They are alkaline to test paper.

1. To some boiling water contained in a test tube add a crystal of $KHCO_3$. It dissolves with effervescence, as bicarbonates are decomposed by heat.

$$2KHCO_3 = K_2CO_3 + OH_2 + CO_2.$$

2. To solution of $MgSO_4$ add solution of $KHCO_3$ made with cold water. No precipitate is formed until the liquid is boiled. The normal carbonate gives an immediate white precipitate ($MgCO_3$).

3. To solution of $HgCl_2$ add solution of $KHCO_3$, prepared with cold water. A yellowish white precipitate is thrown down. The normal carbonate gives a red precipitate.

A. Sulphites. Take sodium sulphite, Na_2SO_3.

1. Sulphites generally resemble carbonates in solubility.

2. All sulphites are decomposed by dilute H_2SO_4, with effervescence if the solution is strong. The escaping gas (SO_2) smells of burning sulphur.

3. When a small quantity of a sulphite or of sulphurous acid has to be recognised the following is the best test :—

Add to a few pieces of granulated zinc contained in a test tube some dilute HCl till there is brisk effer-

vescence. Then pour in a little of the liquid to be tested, and hold a lead acetate test paper in the escaping hydrogen. Any sulphite present will be reduced by the nascent hydrogen and converted into H_2S, which will stain the paper.

$$H_2SO_3 + 6H = H_2S + 3OH_2.$$

B. Theiosulphates. Take sodium theiosulphate (hyposulphite), $Na_2S_2O_3.5OH_2$ dissolved in water.

1. HCl, or dilute H_2SO_4, causes in a minute or two, or immediately on warming, a smell of SO_2 and a yellow precipitate of sulphur.

2. $AgNO_3$; a nearly white pp. ($Ag_2S_2O_3$), which, on shaking, re-dissolves in excess of $Na_2S_2O_3$. Add excess of $AgNO_3$ and heat; the pp. becomes black.

$Ag_2S_2O_3$	+	OH_2	=	Ag_2S	+	H_2SO_4.
Silver theiosulphate.				Silver sulphide.		Sulphuric acid.

A. Sulphides.

1. All sulphides are insoluble in water, except those of Ba, Sr, Ca, Mg, K, Na, NH_4.

2. Nearly all sulphides are decomposed by hydrochloric acid, and by dilute sulphuric acid, evolving H_2S, which is known by the smell and by blackening lead test paper.

Exceptions :—

As_2S_3, insoluble in hot strong HCl.
HgS „ „ „
FeS_2 (iron pyrites) „ „
CuS, almost insoluble.

Ag_2S, NiS, and CoS, insoluble in dilute HCl, decomposed with difficulty by strong HCl.

3. When any sulphide is heated with HCl mixed with HNO_3 or $KClO_3$, the sulphur gradually dissolves in the form of H_2SO_4, which may be recognised by adding $BaCl_2$.

4. A dry sulphide, heated in an open test tube, or, better, in a piece of hard glass tubing open at both ends and held obliquely over a flame, generally gives by oxidation sulphur dioxide gas, which is easily recognisable by the smell.

B. Hypochlorites.—Not known except in combination or mixture with the chloride of the same metal. Bleaching powder, or 'chloride of lime' ($CaCl_2.CaCl_2O_2$, or, more probably, CaCl(ClO)), may be taken as an example.

Shake up some bleaching powder with cold water, and filter the liquid.

1. H_2SO_4; chlorine evolved, recognisable by smell, colour, and bleaching power.

$$CaCl(ClO)+H_2SO_4=CaSO_4+OH_2+Cl_2.$$

2. $Pb(C_2H_3O_2)_2$; a white pp., becoming yellow, and then deep brown, especially when heated. The brown pp. is lead peroxide, PbO_2.

B. Nitrites.

Take potassium nitrite, KNO_2.

1. Dilute H_2SO_4 ; yellow gas (N_2O_3) evolved. A nitrate mixed with dilute sulphuric acid gives off no gas.

2. KI, mucilage of starch, dilute H_2SO_4, added successively ; a blue colour, showing liberated iodine. Nitrates give no colour with the same reagents.

3. In other respects nitrites agree with nitrates.

B. Cyanides.

Take solution of potassium cyanide, KCN.

1. Dilute H_2SO_4 added to a very small quantity of KCN gives a peculiar disagreeable smell of HCN (hydrocyanic acid or prussic acid). *This vapour is to be carefully avoided, as it is very poisonous.*

2. Solution of $FeSO_4$, then Fe_2Cl_6 and excess of dilute HCl ; deep blue pp. (prussian blue).

3. A minute quantity of a cyanide dissolved in a few drops of yellow $(NH_4)_2S_2$ gives ammonium theiocyanate, NH_4CNS. Evaporate till excess of sulphide is driven off, then dilute, and add Fe_2Cl_6 and a very little HCl ; blood-red coloration, ferric theiocyanate ($Fe_2C_6N_6S_6$).

4. $AgNO_3$ added to KCN gives a pp. (AgCN) which at first re-dissolves, but remains when excess of

$AgNO_3$ has been added. Collect the precipitate on a filter, wash, dry, and heat it to redness. Metallic silver remains. Silver chloride, AgCl, when heated, melts, but is not decomposed.

SECOND DIVISION.

Salts which are not perceptibly decomposed by cold dilute H_2SO_4, but are decomposed by hot strong H_2SO_4, evolving gas or vapour.

Nitrates	evolve	HNO_3
Chlorides	„	HCl
Bromides	„	HBr and Br_2
Iodides	„	I_2
Fluorides	„	HF
Chlorates	„	ClO_2
Acetates	„	$HC_2H_3O_2$
Oxalates	„	CO_2+CO
Tartrates	„	CO, SO_2, &c.
Ferrocyanides	„	CO
Ferricyanides	„	CO.

A. Nitrates.

Examples of Common Nitrates:—

Nitre or saltpetre . .	KNO_3
Chili nitre or saltpetre .	$NaNO_3$
Silver nitrate . . .	$AgNO_3$
Barium nitrate . .	$Ba(NO_3)_2$.

Take potassium nitrate, KNO_3.

1. All nitrates are soluble in water (except a few oxynitrates—e.g. $BiONO_3$).

2. Strong H_2SO_4 heated with a solid nitrate, or with a strong solution; acid fumes of HNO_3. Copper scraps added cause the evolution of NO, which becomes orange red on mixing with the air.

3. Take a weak solution of the nitrate, and dissolve in it a crystal of $FeSO_4.7OH_2$. When quite cold pour into the tube, held slanting, sufficient strong H_2SO_4 to form a distinct layer at the bottom. A deep purplish or brown colour will appear where the two liquids meet.

4. Melt a nitrate on charcoal; it deflagrates (see pp. 22, 28).

A. Chlorides.

Examples of Common Chlorides :—

Common salt . .	NaCl
Potassium chloride .	KCl
Calcium chloride .	$CaCl_2$ or $CaCl_2.6OH_2$
Barium chloride .	$BaCl_2.2OH_2$.

Take sodium chloride, NaCl.

1. All chlorides are soluble in water except AgCl, Hg_2Cl_2, and a few oxychlorides—e.g. BiOCl, SbOCl.

2. Strong H_2SO_4 added to a solid chloride or to a strong solution of a chloride; steamy acid fumes of HCl are evolved.

3. Add a little water and MnO_2 to the residue

of test 2 ; chlorine evolved, which bleaches wet litmus paper.

4. $AgNO_3$ added to the solution of NaCl; a white curdy pp., insoluble in boiling strong HNO_3 (AgCN dissolves), soluble in solution of ammonia.

B. Bromides.

Take potassium bromide KBr.

1. All bromides are soluble in water except AgBr, Hg_2Br_2, $PbBr_2$ (sparingly soluble).

2. Strong H_2SO_4; steamy fumes of HBr accompanied by brown vapour of bromine, the quantity of which is increased by adding MnO_2.

3. Add chlorine water to the solution ; the liquid becomes yellow from free bromine. Shake up with a little CS_2 and let it stand. An orange-coloured solution of bromine in CS_2 sinks to the bottom.

4. $AgNO_3$ added to the solution gives a yellowish-white pp., AgBr, which is insoluble in nitric acid, but somewhat soluble in ammonia.

A. Iodides.

Use potassium iodide KI.

1. All common iodides are soluble in water except AgI, HgI_2, Hg_2I_2, PbI_2 (sparingly soluble), Cu_2I_2.

2. Strong H_2SO_4, poured into the solution, gives a brown liquid, which deposits black scales of iodine, and as it becomes hot evolves purple vapour.

3. Chlorine water ; a brown liquid, which shaken

up with carbon bisulphide gives a purple solution of iodine, which rapidly settles to the bottom, leaving the watery liquid partly or wholly decolorised.

4. Starch solution followed by a few drops of chlorine water, or of bromine water, or of potassium nitrite and sulphuric acid ; an intensely blue compound of iodine and starch. The blue colour is destroyed by heat or by excess of chlorine or bromine, but not by the nitrite.

5. $AgNO_3$; a yellow pp. (AgI) insoluble in nitric acid, and almost insoluble in solution of ammonia.

6. $HgCl_2$; a scarlet pp. (HgI_2), soluble in excess either of $HgCl_2$ or of KI.

$HgCl_2$ gives no pp. with a chloride or bromide.

B. Fluorides.

The only fluorides of importance are fluor spar, CaF_2, and cryolite, Na_3AlF_6. These are both insoluble in water and dilute acids.

The test for fluorides depends upon their decomposition by sulphuric acid, and the action of the resulting HF upon glass.

Into a small leaden cup a little powdered fluor spar is put, and moistened with a few drops of strong H_2SO_4. A piece of glass is coated with paraffin or wax, a few marks scratched through the wax so as to lay bare a portion of the glass, and this prepared surface is then exposed to the fumes produced by gently heating the fluor spar and sulphuric acid. Care

should be taken that the wax is not melted. After a few minutes the glass is removed, the wax cleaned off, and the exposed portions of the surface will be found to be permanently etched.

B. Chlorates.

Take potassium chlorate, $KClO_3$.

1. All ordinary chlorates are soluble in water.

2. Strong H_2SO_4; a few crystals wetted with the acid become yellow and give off a yellow gas (ClO_2). On applying heat a succession of explosions occurs.

3. Heat the dry salt; oxygen is evolved. On charcoal it deflagrates like a nitrate.

4. Heat a small crystal till boiling ceases, cool, dissolve in water, and add $AgNO_3$; white pp. of AgCl. (Difference from nitrate.)

A. Acetates.

Examples of Common Acetates:—

Potassium acetate .	$KC_2H_3O_2$
Sodium acetate . .	$NaC_2H_3O_2.3OH_2$
Sugar of lead . .	$Pb(C_2H_3O_2)_2.3OH_2$

Take sodium acetate.

1. All acetates are soluble in water. $AgC_2H_3O_2$ and $Hg_2(C_2H_3O_2)_2$ are the least soluble.

2. Strong H_2SO_4, gently heated with a solid acetate or with a strong solution of the same; a smell of strong vinegar.

3. Add to the residue of test 2 a few drops of rectified spirit; a fragrant smell of ethyl acetate is produced on heating.

4. A solid acetate heated evolves a mixture of acetic acid and acetone. Smell characteristic.

5. Fe_2Cl_6 added to the solution in water; an orange-red coloration, giving a brown pp. (basic ferric acetate) on boiling.

A. Oxalates.

Examples of Common Oxalates:—

Oxalic acid . .	$H_2C_2O_4.2OH_2$
Ammonium oxalate .	$(NH_4)_2C_2O_4.2OH_2$
Salt of sorrel . .	$\left\{\begin{matrix}KHC_2O_4\\H_2C_2O_4\end{matrix}\right\}2OH_2.$

Take ammonium oxalate.

1. Most oxalates are insoluble in water except the oxalates of the alkali metals. There are acid and neutral oxalates.

2. Strong H_2SO_4, added to a solid oxalate or to a strong solution of the same; on applying heat effervescence occurs, due to escape of a mixture of CO and CO_2. The former is combustible, and when in sufficient quantity will burn at the mouth of the tube. The latter can be recognised by its action on lime water.

Test for it as in dealing with a carbonate, p. ;

3. Dilute H_2SO_4; no effervescence even

heated, but an immediate evolution of CO_2 on adding a little MnO_2.

4. Action of heat on oxalates.

Dry $(NH_4)_2C_2O_4$, when heated in a test tube, gives a sublimate of oxamide, $C_2O_2(NH_2)_2$, which is nearly insoluble in water.

Other oxalates give first inflammable CO, and afterwards CO_2, or a mixture of the two gases. The residue is sometimes grey, but never black.

A. Tartrates.

Examples of Common Tartrates:—

Tartaric acid . .	$H_2C_4H_4O_6$
Potassium neutral tartrate	$K_2C_4H_4O_6$
Cream of tartar . .	$KHC_4H_4O_6$
Sodium acid tartrate .	$NaHC_4H_4O_6.OH_2$
Rochelle salt . .	$KNaC_4H_4O_6.4OH_2$
Tartar emetic . .	$K(SbO)C_4H_4O_6.OH_2$

Take Rochelle salt.

1. Very many tartrates are soluble in water, and the presence of tartaric acid in a solution prevents the precipitation of some metals—e.g. Fe, Cr, Al—by alkalies.

2. Strong H_2SO_4; on applying heat, charring occurs, and a mixture of gases—SO_2, CO_2, CO, &c.—is evolved.

3. $AgNO_3$ added to the solution in water; a white pp. of $Ag_2C_4H_4O_6$, soluble in a few drops of HNO_3. Heat gently for some time; a black pp.

of metallic silver is formed, partly deposited upon the tube as a shining silvery coating.

4. Heat the dry salt; a smell of burnt sugar is evolved, and the residue becomes black from production of charcoal.

B. Ferrocyanides.

The only soluble ferrocyanide commonly met with is the potassium ferrocyanide, or yellow prussiate of potash, $K_4FeC_6N_6.3OH_2$. It forms large yellow crystals, easily recognisable by their ready cleavage in one direction.

1. Dilute H_2SO_4; no change when added to the cold solution in water. On boiling, vapour of HCN is evolved, and the liquid becomes blue. Remember that HCN is poisonous.

2. Strong H_2SO_4; added to the dry salt and heat applied, a white mass of potassium sulphate, ammonium sulphate, and ferrous sulphate is formed, and abundance of carbonic oxide, CO, is evolved.

$$K_4FeC_6N_6 + 11H_2SO_4 + 6OH_2 = 4KHSO_4 + 6NH_4HSO_4 + FeSO_4 + 6CO.$$

3. Solution of $FeSO_4$, free from ferric salt; added to the solution gives a white pp., which rapidly becomes blue on exposure to the air.

4. Fe_2Cl_6; added to the solution gives 'prussian blue.'

5. $CuSO_4$; gives reddish-brown cupric ferrocyanide.

B. Ferricyanides.

The only common ferricyanide is the potassium salt, 'red prussiate of potash,' $K_6Fe_2(CN)_{12}$.

1. Dilute H_2SO_4; HCN evolved on boiling. Remember that HCN is poisonous.

2. Strong H_2SO_4 and a few drops of water; CO evolved, accompanied by a small quantity of CO_2.

3. Solution of $FeSO_4$; a deep blue pp., 'Turnbull's blue.'

4. Solution of Fe_2Cl_6; no pp., but a deep brown or greenish coloration.

THIRD DIVISION.

Salts which give no gas or vapour when heated with strong H_2SO_4.

Sulphates
Phosphates
Arseniates
Borates
Chromates (evolve a little oxygen).

A. Sulphates.

Examples of Common Sulphates:—

Potassium sulphate	K_2SO_4
Sodium sulphate	$Na_2SO_4.10OH_2$
Gypsum . .	$CaSO_4.2OH_2$
Green vitriol .	$FeSO_4.7OH_2$
Blue vitriol .	$CuSO_4.5OH_2$
Epsom salt .	$MgSO_4.7OH_2$

Zinc sulphate .	$ZnSO_4.7OH_2$
Alum . .	$(NH_4)_2SO_4.Al_2(SO_4)_3.24OH_2$

or

$$K_2SO_4.Al_2(SO_4)_3.24OH_2.$$

Take sodium sulphate.

1. All sulphates are soluble in water except $BaSO_4$, $PbSO_4$, $SrSO_4$, $CaSO_4$. The last is slightly soluble.

2. $BaCl_2$ added to the solution in water; a white pp. insoluble in HCl.

3. Mix the dry salt with some powdered charcoal, moisten with water, and then fuse in the inner flame on charcoal. The fused mass contains sodium sulphide, Na_2S. If the mass is wetted and placed on a silver coin, it makes a dark brown stain, and when treated with dilute HCl it evolves H_2S.

If a sulphate containing a heavy metal (such as Fe) is to be tested, it must be mixed with some Na_2CO_3 before heating.

A. Phosphates.

Examples of Common Phosphates:—

Sodium phosphate .	$Na_2HPO_4.12OH_2$
Microcosmic salt .	$NaNH_4HPO_4.4OH_2$
Bone phosphate .	$Ca_3(PO_4)_2$
Superphosphate of lime	$CaH_4(PO_4)_2$.

Take sodium phosphate.

1. All phosphates are insoluble in water except the phosphates of the alkali metals and a few acid salts.

2. $AgNO_3$ added to the solution in water; a yellow pp. (Ag_3PO_4) soluble in NH_4HO and in acids.

3. A large excess of NH_4HMoO_4 dissolved in nitric acid; a yellow liquid which on heating deposits a yellow pp.

This pp. is not formed readily in presence of much phosphate or of hydrochloric acid. This test is applicable to all phosphates.

4. Mix NH_4Cl, $MgSO_4$, and excess of NH_4HO; this solution added to an alkaline phosphate gives a white pp., $MgNH_4PO_4.6OH_2$. Compare magnesium, p. 46.

B. Arseniates.

Take sodium arseniate, $Na_2HAsO_4.7OH_2$.

1. Arseniates resemble phosphates in nearly every respect as regards solubility.

2. $AgNO_3$ added to the solution in water; a chocolate brown pp. (Ag_3AsO_4), soluble in NH_4HO and in acids.

3. A large excess of acid ammonium molybdate gives a pp. as with a phosphate, but only on boiling.

4. Mixture of $MgSO_4$, NH_4Cl, and NH_4HO; white pp., $MgNH_4AsO_4.6OH_2$ resembling the phosphate.

5. Add strong HCl, then heat to boiling, and pass H_2S; a yellow pp. of As_2S_3 mixed with sulphur is thrown down.

(Difference from phosphate.)

B. Borates.

Take common borax, $Na_2B_4O_7.10OH_2$.

1. Borates are generally insoluble in water, except the borates of the alkali metals. Common borax, though acid in constitution ($Na_2B_4O_7OH_2 = 2NaBO_2.HBO_2$), is alkaline to test paper.

2. Add HCl to solution of borax, wet a piece of turmeric paper with the solution, and dry it in a water bath. It is stained red. Moisten the stain with solution of soda; it becomes deep blue.

3. Mix a few drops of strong sulphuric acid into a paste with borax, then add some methylated spirit, and set fire to it in a dark place. The flame is tinged green.

B. Chromates.

Take potassium chromate, K_2CrO_4, dissolved in water.

1. All chromates are red or yellow. Nearly all except the chromates of K, Na, NH_4, Ca, are insoluble in water.

2. $AgNO_3$; red pp. (Ag_2CrO_4).

3. $Pb(C_2H_3O_2)_2$; yellow pp. ($PbCrO_4$).

4. Dilute H_2SO_4; the colour of the solution deepens, owing to formation of chromic acid. Now add sulphurous acid; the solution becomes green from reduction.

$$\underset{\text{Chromic anhydride.}}{2CrO_3} + \underset{\text{Sulphurous acid.}}{3H_2SO_3} = \underset{\text{Chromic sulphate.}}{Cr_2(SO_4)_3} + \underset{\text{Water.}}{3OH_2}.$$

5. Other 'reducing' agents may be used instead of H_2SO_3; for example, H_2S (sulphur precipitated), alcohol (aldehyd given off on boiling), oxalic acid (CO_2 evolved).

Note.—Chromates, when heated strongly with sulphuric acid, evolve oxygen. This character, however, is not easily available as a test.

SPECIAL TREATMENT OF PHOSPHATES INSOLUBLE IN WATER.

B. When an unknown substance or mixture of substances is to be examined by the table, p. 74, it is necessary, in the absence of information about it, to ascertain whether phosphates are present or not. This is done by applying the molybdic acid test to the nitric acid solution. If phosphates are found, the treatment of the solution after removal of the H_2S precipitate must be modified; because, if either of the alkaline earth metals, Ba, Sr, Ca, Mg, is present, it will be thrown down in the form of phosphate when the solution is neutralised by NH_4HO, unless a sufficient quantity of Fe, Al, or Cr is present to decompose those salts completely. If, however, there is excess of Fe, Al, or Cr, the presence of phosphoric acid merely leads to the precipitation of part of these metals as phosphates, whilst the earthy metals find their proper

place in the scheme. The principle of the process, then, lies in adding to the filtrate from the H_2S group a slight excess of ferric chloride, and then precipitating in the presence of acetic acid, in which ferric phosphate is insoluble. The excess of iron in the form of acetate is got rid of by boiling the liquid, when the ferric acetate splits up into acetic acid, which remains in solution, and a basic or oxy-acetate of iron, which is precipitated.

If the object is merely to recognise the metal contained in a phosphate of this kind, the following methods may be used :—

1. Dissolve a portion of the phosphate in hydrochloric acid, and add dilute sulphuric acid in excess. Heat gently. If a pp. appears immediately, the metal is probably Ba; if only on heating, it is probably Sr. If no pp. appears at all, the metal may be Ca or Mg. Collect and wash the pp. Dry the filter, and burn it in a coil of platinum wire till the ash is nearly white. The sulphate is thus partly reduced to sulphide. Moisten the ash with HCl and test it by the flame and spectroscope.

2. If no pp. is formed by H_2SO_4, the following process must be used:—

Dissolve the substance in a little dilute HCl in a beaker; add a slight excess of $Na\bar{A}$, in crystals, and a little acetic acid; then pour in solution of Fe_2Cl_6 till there is not only a pp. ($Fe_2(PO_4)_2$), but the liquid is coloured brown from formation of ferric acetate. Boil

gently in the beaker for five minutes, and filter hot. Divide the filtrate into several parts.

a. Add NH_4Cl, NH_4HO, and $(NH_4)_2CO_3$. Heat gently. If no pp. forms, add Na_2HPO_4; white pp. indicates Mg.

b. If a pp. is formed by the carbonate, add to a fresh portion of the solution $CaSO_4$.

Immediate pp.	indicates	Ba
Pp. only on boiling	„	Sr
No pp. on boiling	„	Ca.

c. If a pp. is formed by the carbonate, confirm by collecting it on a filter, washing it with hot water, re-dissolving in a drop or two of HCl, and testing by flame and spectroscope.

GENERAL DIRECTIONS FOR ANALYSING AN UNKNOWN SUBSTANCE.

Notes are always to be made in the following order, and must invariably be written down immediately after making each experiment, and are not to be left till the end:—

PRELIMINARY.

1. DESCRIPTION of the substance—solid or liquid, colour, crystalline form, action on test papers. (See Memoranda I. and II., end of the book.)

2. HEAT IN SMALL DRY TUBE. Result—fusion, water or solid sublimate, change of colour, gas evolved. (See Tables II. and III., end of the book.)

3. DISSOLVE in water if possible ; if not, dissolve in HCl, in HNO_3, or in aqua regia. (See Memoranda I. and IV.) If not soluble refer to p. 99.

4. OBSERVE COLOUR GIVEN TO FLAME by a particle held on platinum loop—yellow, orange red, crimson, yellowish green, bright green, blue, violet.

Use the spectroscope for recognition of K, Sr, &c.

DETECTION OF THE METALLIC RADICLES.

5. ADD GROUP TESTS TO THE ORIGINAL solution, proceeding according to table already learnt (p. 74).

I. HCl
II. $HCl + H_2S$
III. $NH_4Cl + NH_4HO$

Note.—If a white or pale-coloured pp. is formed here, it may consist of $Al_2(HO)_6$, $Al_2(PO_4)_2$, or phosphate or oxalate of Ba, Sr, Ca, Mg.

Take a fresh portion of the solution from which the pps. produced by HCl and H_2S have been removed, add NaHO, and observe whether the pp. which is formed dissolves in excess. A white pp. which re-dissolves consists of $Al_2(HO)_6$ or $Al_2(PO_4)_2$ or Zn $(HO)_2$.

If it does not re-dissolve, test the original substance by molybdate of ammonium. If it prove to contain a phosphate, the filtrate from the H_2S group must be boiled, first alone to expel H_2S, then with a few drops of HNO_3. Excess of $Na\bar{A}$, some $H\bar{A}$, and solution of Fe_2Cl_6 should then be added in succession, and the liquid boiled, as directed p. 95. After filtering the hot liquid, NH_4HO is added in slight excess, and if a pp. is produced this may be filtered off, added to the pp. previously obtained by boiling and the whole tested for Al and Cr. The analysis may then be finished by adding the remaining group tests, NH_4HS, &c.

If the substance is not a phosphate, test the original for an oxalate. If an oxalate is found, heat some of the original solid strongly, so as to convert it into carbonate or oxide; then dissolve this in HCl and test for the metal in the usual way.

IV. NH_4HS
V. $(NH_4)_2CO_3$
VI. Na_2HPO_4
VII. Tests for K, Na, NH_4, H.

If no other positive radicle can be found, and the solution reddens litmus, the compound is probably a hydrogen salt; that is, an acid. All common acids when heated strongly evaporate or burn away, leaving no residue, except H_3PO_4, which leaves HPO_3; H_3AsO_4, which leaves As_2O_5, volatile at a red heat; H_3BO_3, which leaves B_2O_3; and CrO_3 which leaves Cr_2O_3.

6. Having found the metallic radicles, proceed to apply CONFIRMATORY TESTS by heating before the blowpipe, on charcoal, or in borax bead, &c.

7. Look for indications of the VALENCY of the metal, should it prove to be Hg, As, Sn, Fe, &c.

DETECTION OF THE NEGATIVE RADICLES.

8. To the original substance add DILUTE H_2SO_4, and heat gently.

Evolution of CO_2 indicates a carbonate.
„ SO_2 a sulphite or theiosulphate.
„ H_2S a sulphide.
„ Cl_2 a hypochlorite.
„ N_2O_3 a nitrite.
„ HCN a cyanide.

9. To the original solid substance add STRONG SULPHURIC ACID, and heat.

Evolution of acid fumes may indicate a chloride, nitrate, or fluoride.

„ brown vapour—a bromide.

„ purple vapour—an iodide.

„ yellow detonating gas—a chlorate.

„ smell of vinegar—an acetate.

„ colourless combustible CO—an oxalate, cyanide, ferrocyanide or ferricyanide.

Blackening indicates a tartrate.

10. Test the solution for a SULPHATE.

11. Test the solution for a PHOSPHATE.

12. Test for a BORATE.

13. Apply CONFIRMATORY TESTS for the negative radicles.

14. Write down the names of the constituents detected, and, if a simple salt, its formula.

ANALYSIS OF SUBSTANCES INSOLUBLE IN HYDROCHLORIC ACID AND IN NITRIC ACID.

List of Insoluble Substances (*those in brackets slightly soluble*):—

$BaSO_4$ $SrSO_4$ ($CaSO_4$, $PbSO_4$)

($PbCl_2$, $PbBr_2$, PbI_2)

(AgCl, AgBr, AgI, very slightly)

Sb_2O_4 and Sb_2O_5
SnO_2
CaF_2
SiO_2 and most silicates
$FeCr_2O_4$

Hg_2Cl_2, Hg_2I_2, HgI_2, HgS, As_2S_3 — soluble in aqua regia and detected in the usual course already given.

1. Moisten the powdered substance with water, take up a small portion on the platinum loop, and hold it in a reducing flame for a few minutes. Cool, moisten the residue with HCl, and introduce it into the Bunsen flame. Characteristic colours given by Ba, Sr, Ca, Pb.

2. Test for sulphate by blowpipe test.

3. Test for Ag, Pb, Sn, Sb, by fusion on charcoal with KCN in reducing flame.

4. Test for SiO_2 thus :—Make a clear bead of sodium metaphosphate by heating microcosmic salt on a platinum loop. Fuse a particle of the substance in the bead by the aid of the blowpipe flame. If silica is present, it will float about undissolved, no matter how long it is heated; whilst the metallic oxides present will dissolve, some of them (especially Cr_2O_3) communicating characteristic colours to the bead.

A more satisfactory process is as follows:—Powder the substance finely, mix with at least four times its weight of $NaHCO_3$ and a little KNO_3, and fuse in a

platinum capsule for five to ten minutes. Cool, boil the capsule with its contents in water, filter, and test the liquid for SiO_2 by acidifying with HCl, evaporating just to dryness, and treating the residue again with HCl. SiO_2 remains as a gelatinous substance insoluble in acids.

If SiO_2 is not found, test the liquid for CrO_4, SO_4, Cl, Br, I. The insoluble residue must be washed with hot water and boiled with HCl, which will dissolve at least part of it. The solution can be tested for the metals.

5. Test for F.

6. Carbon or sulphur may occasionally occur. These are recognised by characters already given (pp. 28, 29, 30).

TABLES OF MEMORANDA.

I.

Remember that solutions of

Copper salts	are	generally	green or blue.
Ferrous	„	„	pale green, becoming rusty.
Ferric	„	„	yellow or brown.
Chromic	„	„	green or violet.
Cobalt	„	„	pale red.
Nickel	„	„	green.
Manganese	„	„	very pale red.

Also that all the chromates are red or yellow.

Salts of other common metals are generally colourless.

All common nitrates, acetates, sulphates, chlorides, bromides, iodides (with the exceptions already given under these heads respectively), are soluble in water. Carbonates and phosphates, except those of the alkali-metals, are insoluble in water, but are soluble in dilute acids.

Oxides and hydroxides are generally insoluble in water, except KHO, NaHO, $Ba(HO)_2$, $Ca(HO)_2$, which are strongly alkaline, and As_2O_3 and As_2O_5, which yield acid solutions.

APPENDIX.

To Recover Silver from Residues.

Add a slight excess of hydrochloric acid and allow the precipitated chloride of silver to subside. Pour away the supernatant liquid and wash the precipitate several times with water. Drain the chloride well, place it in an evaporating dish, stir it up with a small quantity of dilute sulphuric acid, leaving it in the form of a paste. Then lay upon the mass a clean sheet of zinc, and leave it undisturbed for twenty-four hours. At the end of this time remove the zinc, collect the spongy mass of silver upon a filter, and wash it well with hot water. It may then be dissolved in nitric acid and converted into nitrate, or it may be dried and melted into a button. Any chloride remaining unreduced, together with the scrapings of the zinc plate, should be returned to the bottle reserved for residues.

To Recover Platinum from Residues.

Evaporate the whole, liquid and solid together, to dryness. Place the dry residue in a crucible, and heat it to redness so that the platinum may be reduced to the

metallic state, and all organic matter distroyed. Boil the black mass in hydrochloric acid, then in water, then in nitric acid, and finally in water again. Wash the residue well in water and throw away all these liquids. Heat the solid which remains with a small quantity of *aqua regia* till all the platinum is dissolved. Wash any carbonaceous matter that remains, add the washings to the solution and evaporate the liquid to dryness on a water-bath. Pure platinum perchloride, $PtCl_4$, remains.

Separation of the Fourth Group from the Third Group of Metals.

The process given in the table (p. 75) is chosen for general use on account of its simplicity, but when small quantities of zinc or manganese have to be tested for in the presence of much iron or chromium, the process fails on account of the tendency of ferric and chromic hydroxides to carry down in a loose state of combination the hydroxides of these metals.

In such case the following method of separation must be used.

To the filtrate from the H_2S group add NH_4Cl, NH_4HO, and NH_4HS. The precipitate, which contains all the metals of groups III. and IV., is collected, washed, and dissolved in HCl, with the aid of a few drops of HNO_3 or a crystal of $KClO_3$. The solution is then boiled till all smell of chlorine has disappeared. The object of this is to decompose manganic chloride into manganous chloride and free chlorine. The liquid is then mixed in a flask with NaHO till, on shaking, the precipitated hydroxide is only slowly re-dissolved, and the liquid remains slightly acid. Pure precipitated barium carbonate is then added in slight excess, the flask corked,

and the mixture shaken and gently warmed during a quarter of an hour. The liquid is then filtered.

Precip. =
$Fe_2(HO)_6$,
$Cr_2(HO)_6$,
$Al_2(HO)_6$,
with excess of $BaCO_3$.

Wash well, dissolve in HCl, reprecip. with NH_4HO, and separate in the usual way (pp. 58–59.)

Filtrate. — Co, Ni, Mn, Zn chlorides, together with $BaCl_2$. Add dilute H_2SO_4 in slight excess, filter off the $BaSO_4$, and separate the metals in the usual way (pp. 53–54).

Additional Tests for Chloride, Bromide, and Iodide.

Chloride.—Mix a small quantity of common salt with about six times its weight of potassium dichromate, and put the mixture into a dry test-tube (fig. 9, *a*). Select a piece of glass tubing just so wide that, with the aid of half an inch of india-rubber tubing (*b*) slipped over it, it

Fig. 9.

will fit into the mouth of the test-tube. Let this glass tube be about 9 inches long and bent near the middle to a right angle. Now pour a little strong sulphuric acid upon the powder, fit in the tube, as shown in the sketch, and take a second test-tube (*c*) as receiver. On applying a gentle heat a red vapour will be evolved, which should

be passed into a little water placed in the receiver. This vapour is chromyl dichloride, CrO_2Cl_2—

$$4NaCl + K_2Cr_2O_7 + 6H_2SO_4 = 2CrO_2Cl_2 + 4NaHSO_4 + 2KHSO_4 + 3H_2O,$$

and $$CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl.$$

Add to the solution a slight excess of ammonia. The liquid remains yellow, forming a mixture of chromate and chloride.

The presence of the chromate can be further proved by acidifying with acetic acid and adding excess of $AgNO_3$. The presence of chromate in the distillate is a sign of the presence of chloride in the original substance, since bromides under the same circumstances yield only bromine, and iodides only iodine.

Bromide.—Repeat the foregoing experiment, using KBr in place of the NaCl. A brown vapour is obtained and a yellowish solution in the receiver, but on adding ammonia to this it effervesces (from escape of nitrogen) and is completely decolorised—

$$3Br_2 + 2NH_4HO = N_2 + 2H_2O + 6HBr.$$

Iodide.—Add to a solution of iodide of potassium solution of copper sulphate. A dirty-white precipitate of cuprous iodide is formed, and the liquid becomes brown from liberated iodine—

$$4KI + 2CuSO_4 = 2K_2SO_4 + Cu_2I_2 + I_2.$$

Add to the liquid solution of sulphurous acid and a little more copper sulphate. The liquid loses the brown colour and remains green. The precipitate then contains all the iodine in the form of cuprous iodide—

$$H_2SO_3 + H_2O + I_2 = H_2SO_4 + 2HI.$$
$$2HI + 2CuSO_4 + H_2SO_3 + H_2O = Cu_2I_2 + 3H_2SO_4.$$

Detection of Chloride, Bromide, and Iodide in presence of one another.

Test first for iodide by starch and chlorine water.

I. *Iodide being present, to test for Bromide and Chloride.*—To the solution add excess of $CuSO_4$ and solution of H_2SO_3 till the brown colour is destroyed. Warm the liquid, and if very acid add a few drops of solution of ammonia.

Filter off the Cu_2I_2. Add to the filtrate excess of NaHO, boil, filter off the CuO, and divide the liquid into two parts.

Test one portion for chloride by evaporating to dryness and distilling the residue with potassium bichromate and sulphuric acid. Test the other portion for bromide by acidifying with dilute H_2SO_4, adding a large globule of CS_2, and then chlorine water, a few drops at a time, shaking well after each addition (see p. 84).

II. *Iodide is absent.*—Test for bromide by the use of CS_2 and chlorine water.

If present, chloride must be sought by the method of distillation with bichromate and sulphuric acid.

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